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VOL. 41 No. 373 JANUARY 1955

VAPOUR–LIQUID EQUILIBRIA OF C_7-HYDROCARBON–FURFURAL SYSTEMS†

By F. H. GARNER‡, O.B.E. (Fellow) and R. T. W. HALL§ (Associate Fellow)

PART I. BINARY AND TERNARY DATA FOR THE SYSTEM METHYL*CYCLO*HEXANE–TOLUENE–FURFURAL

SUMMARY

Isobaric vapour–liquid equilibrium data are presented for the system methyl*cyclo*hexane–toluene–furfural, including the constituent binary systems.

Two equilibrium stills were used in determining the experimental data, namely the Fenske and Gillespie stills. All determinations were made at 760 mm pressure, and separate liquid and vapour deviation functions were calculated.

The experimental data were correlated by the Li–Coull method, which has been found to provide a useful criterion of true equilibrium for isobaric data. The ease of separation of methyl*cyclo*hexane and toluene, as measured by the relative volatility, is much increased by the presence of furfural. The optimum solvent concentration is in the region of 90 per cent, whilst an economic solvent concentration would be approximately 60 per cent. A new binary azeotrope is reported involving methyl*cyclo*hexane and furfural. Analytical data for the toluene–furfural binary system, and for the ternary mixtures which are single phase at 20° C, are presented for the first time.

NOMENCLATURE

b	Partial mol volume
k	Constant in Li–Coull equations
n	Refractive index
p	Partial pressure
t	Temperature ° C
v	Partial molar (liquid) volume
x	Mol fraction (liquid phase)
y	Mol fraction (vapour phase)
y^*	Mol fraction (vapour phase)—on solvent free basis
z	Gas phase correction factor
α	Relative volatility
γ	Activity coefficient
Σ	Summation of
π	Total pressure of system

SUBSCRIPTS

1	Refers to component No. 1 (etc.)
i	Refers to component i
c	Critical value
r	Reduced value
H	Heptane
M	Methyl*cyclo*hexane
T	Toluene
F	Furfural
expt	Value as experimentally determined
calc	Value as calculated from correlation equations
log	Logarithm to the base 10
ln	Logarithm to the base e

INTRODUCTION

ONE of the most important developments in the petroleum and allied industries in recent years has been the extended use of petroleum as the raw material for the separation of pure hydrocarbons which are used directly as components of high octane fuel, or alternatively are processed further to give other derivatives. The existence of so many individual hydrocarbons in even a close-boiling petroleum fraction has inevitably delayed the production on a large scale of pure hydrocarbons, because of the difficult separation problems which are involved. The separation by distillation of hydrocarbons of different types, *e.g.* naphthenic and aromatic, can be facilitated by the addition of a third component, generally of a polar nature, which forms solutions with the hydrocarbons of varying degrees of non-ideality. The addition of an extraneous compound forms the basis of both the operations known as "azeotropic" and "extractive distillation," the added component being termed the "entrainer" and "solvent" in the respective operations. Both processes may occur simultaneously. The extractive distillation process has several features in common with the liquid–liquid or "solvent extraction" process, and derives its name from this older process.

The design of plant for separations of this type necessitates prior knowledge of the basic vapour–liquid equilibria of the mixtures to be encountered. This paper presents a study of the equilibria of C_7 hydrocarbons and furfural at normal atmospheric pressure.

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NOMENCLATURE

B	Second virial coefficient
I	Intercept
I'	Average intercept value
P	Vapour pressure of a pure component
R	Gas constant
S	Slope of Li–Coull curves
T	Absolute temperature ° K
X	Molar ratio of components (liquid phase)
X^*	Common mol ratio at point of intersection of Li–Coull curves
Y	$(T \log \gamma)^{-0.5}$
Y'	$(T \log \gamma)^{-0.5}$ at $X = 1$
b	Partial mol volume
k	Constant in Li–Coull equations
n	Refractive index
p	Partial pressure
t	Temperature ° C
v	Partial molar (liquid) volume
x	Mol fraction (liquid phase)
y	Mol fraction (vapour phase)
y^*	Mol fraction (vapour phase)—on solvent free basis
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Under ideal conditions in both liquid and vapour phases, equilibrium data for each component can be correlated by means of Raoult's law :

$$p_i = P_i x_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

giving

$$\pi = P_1 x_1 + P_2 x_2 + \ldots \quad . \quad . \quad . \quad . \quad (2)$$

When the liquid phase displays non-ideal tendencies, such a relationship as (2) fails to hold, and Carlson and Colburn [8] derived a relationship for such cases :

$$\pi = \gamma_1 P_1 x_1 + \gamma_2 P_2 x_2 + \ldots \quad . \quad . \quad . \quad . \quad (3)$$

the activity coefficients γ_1 and γ_2 assuming a value of unity under ideal conditions.

Furthermore, when the vapour phase also departs from ideal behaviour, a second correction factor, z,[44] is incorporated, so that equation (3) becomes modified to give :

$$\pi = \frac{\gamma_1 P_1 x_1}{z_1} + \frac{\gamma_2 P_2 x_2}{z_2} + \ldots \quad . \quad . \quad . \quad . \quad (4)$$

i.e.

$$y_1 = \frac{\gamma_1 P_1 x_1}{z_1 \pi}$$

or

$$y_1/x_1 = \frac{P_1 \gamma_1}{\pi z_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The gas-correction factor z_1 can be expressed as a function only of the total pressure, partial pressure of component 1, the molar (liquid) volume v_1, and the second virial coefficient B_1 in the following manner :

$$\log z = \frac{(P_1 - \pi)(v_1 - B_1)}{2{\cdot}303 \cdot RT} \quad . \quad . \quad (6)$$

For isobaric conditions, π is constant, and P_1, v_1, and B_1 are functions of temperature only, *i.e.* for each component z_1 can be plotted against temperature. To facilitate computation of the gas phase deviation factors, a plot was constructed of z (for each component studied) from 90° to 170° C. (Heptane is included for use in later papers in this series.) Values from the graph were compared with values obtained from Scheibel's nomograph,[36] and excellent agreement was achieved. Such z-factors have been applied previously mainly to isothermal equilibria [17, 26, 30, 33, 41] involving furfural, C_4 hydrocarbons, and water.

Most of the recent vapour–liquid investigations have been carried out under isobaric conditions.[3, 5, 6, 9, 11, 15, 19, 27, 31, 35, 39] Of particular interest is the work of Fenske and co-workers, who determined the equilibria of the system methyl*cyclo*hexane–toluene,[35] and later the effect of aniline on the hydrocarbon binary.[15] Drickamer, Brown, and White [11] investigated the effect of phenol on the same binary under isobaric conditions.

For isothermal systems, several correlation methods have been developed which accurately describe experimental data, particularly the various van Laar and Margules equations as developed by Wohl.[44] As these equations are integrated forms of the Gibbs–Duhem equation, they are strictly valid only at constant temperature, although they are frequently used, with varying degrees of success on data with a considerable range of temperature. Unfortunately, for isobaric systems, all plots of y or γ against the liquid mol fraction are subject to a hidden temperature variable, which can considerably modify the shapes of the curves obtained in such a way that the above correlation methods cease to be useful. Attempts have been made to derive similar equations for isobaric systems, but without success.[22]

However, other types of correlation methods have been derived for such conditions, particularly by White [42] and by Li and Coull.[28] The equations of White, although satisfactory for binary systems, develop an ambiguity characteristic when applied to ternary systems, and hence the later method of Li and Coull was used for correlation of the present data. Their method is based primarily on the simple van Laar equation, with the added condition that

$$(T \log \gamma)_{x_1 x_2} = \text{constant}$$

and involves the plotting of $(T \log \gamma)^{-0{\cdot}5}$ against the mol ratio x_1/x_2, giving straight line plots.

MATERIALS AND APPARATUS

The limited solubility of the systems placed a severe restriction on the type of equilibrium still to be used. The conventional type of Othmer still [32] is unsuited to liquid mixtures which are two-phase at temperatures near the boiling point, and the Fenske still,[15] which was developed for this type of system, was chosen. The main feature of the still is that the condensate receiver is placed inside the main shell of the apparatus, thus maintaining condensate at a temperature not much lower than its boiling point.

A diagram of the still is shown in Fig 1, and both constructional and operational details are to be found elsewhere.[15] Two types of condensate receivers were used, the vacuum-jacketed type requiring a slightly larger shell diameter and height. The source of heat was a nichrome winding, *S*, on the shell exterior of the boiling tube (17 ft 6 inches of 24 gauge, encased in 2-mm Vidaflex glass sleeving). The addition of an extra condenser on the vent line was made to avoid any loss of volatile constituents.

Temperatures were determined by the use of iron–constantan thermocouples of 30 B. and S. gauge glass-covered duplex wire, encased in 3 mm outside dia stainless steel tubing, being connected to a selector board by "Integra" compensating cable, and thus to an "Integra" portable temperature indicator with a range of 0° to 200° C.

Three stills were used and the thermocouples calibrated with pure benzene, water, ethylene glycol monomethyl ether ("methyl cellosolve") and furfuraldehyde. Measurements were accurate to about 0·2° C. A more sensitive means of measurement would have been desirable, but none was readily available at the time.

The non-jacketed type of condensate cup was used mainly for binary mixtures, where the molal latent

heats and the boiling points were similar, *e.g.* for hydrocarbon pairs. For nearly all other mixtures vacuum-jacketed cups were used to prevent re-evaporation of the recycling liquid.

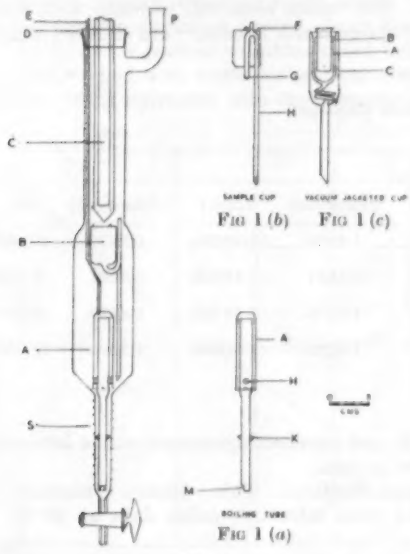

FIG 1 (*b*) FIG 1 (*c*) FIG 1 (*a*)

FIG 1

FENSKE EQUILIBRIUM STILL—CONSTRUCTIONAL DETAILS

A—boiling tube; B—distillate sample cup; C—internal condenser; D—neoprene stopper; E—thermocouple 30 B. and S. gauge, iron–constantan in 3 mm outside dia stainless tube; F—three hooks, 120° apart, for suspending cup from corresponding hooks on condenser; G—drip tip for indicating condensation on sample cup; H—Fig 1 (*a*), two holes 180° apart 5 mm dia, Fig 1 (*b*), vented return leg; K—three nodules, 120° apart, for centering boiling tube; M—opening 5 × 5 mm to facilitate liquid circulation; P—vent line barostat; S—heater winding, 17 ft 6 in of 24 gauge nichrome wire in 2 mm Vidaflex glass sleeving; Fig 1 (*c*), A—sample cup, 25 ml volume, supported in jacket C by three small glass legs, B—funnel to establish liquid passage through A, C—evacuated jacket, suspended from condenser (hooks not shown).

Stopcocks were regularly greased with Dow Corning Silicone "A" valve grease. The stills were periodically cleaned with boiling 4 per cent NaOH solution to remove deposited furfural polymers, and then dried out with boiling crude alcohol, and finally acetone. It is essential to exclude all moisture from the still, and a calcium chloride drying tube 6 × ¼ inch was placed between the vent condenser and the source of constant pressure. Each still was vented to a manifold, itself connected to a ballast tank, maintained at 760 ± 0·5 mm Hg by means of a barostat system incorporating a manostat.[20]

All heating was electrical, from A.C. mains transformed to 110 volts, in order to use moderately robust heating wire (24 or 26 gauge). The wire was glass-sleeved, and covered with a layer of asbestos. Heat input to the stills was controlled by variable rheostats placed in series with the heater unit.

The Fenske stills were found to be satisfactory for all systems, with the exception of those mixtures where the difference in boiling point between liquid charge and vapour condensate was greater than 25° C. Such conditions arise in the moderately non-ideal toluene–furfural binary system and also in very high concentrations (greater than 85 per cent) of furfural with methyl*cyclo*hexane.

As the former system is entirely miscible at 20° C, it was re-investigated, using a Gillespie type of still [18] which had been modified by Ellis [12] as shown in Fig 2. The main modification to the original design was the incorporation of a long residual liquid return line, including a U-tube with a sampling cock, and a cooling leg. Optimum conditions exist in this still for the separation of liquid and vapour phases which are at equilibrium, and both phases are sampled before any re-combination can occur. A full description of this still is given elsewhere.[12]

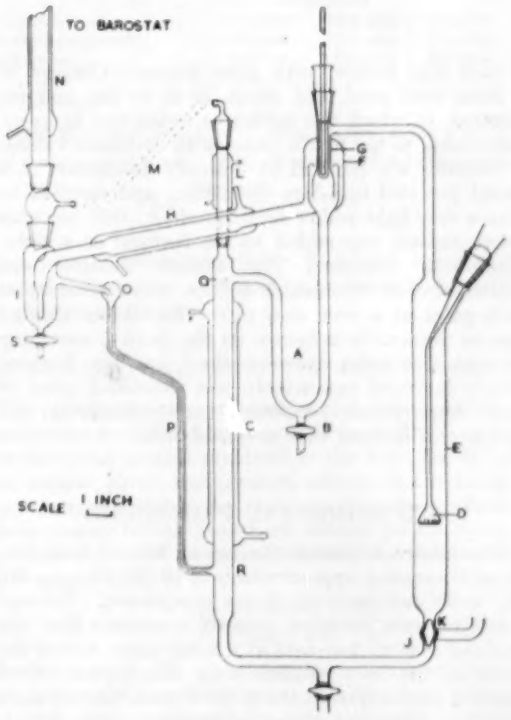

FIG 2

THE MODIFIED GILLESPIE STILL—CONSTRUCTIONAL DETAILS

A—U-tube incorporated into liquid return line; B—sampling cock (liquid); C—liquid stream cooler; D—internal heater; E—Cottrell pump leg; F—adiabatic disengaging chamber; G—thermometer pocket; H—condenser; I—condensate receiver; J—recycle liquid inlet to heating leg; K—main cock for adjusting liquid inventory; L—vent condenser; M—pressure equalizer; N—vent condenser; O—drop counter; P—capillary tube to damp out liquid level fluctuations; Q—normal liquid level during operation; R—recycle liquid return line; S—vapour condensate sampling cock.

MATERIALS EMPLOYED

All relevant details regarding the materials employed, their source, and eventual purity are summarized in Table I.

Both toluene and methyl*cyclo*hexane were purified by batch fractionation on a thirty-plate column of 1 inch dia, packed with glass helices. Charges of 2 litres were used, and about 70 to 80 per cent recovered, of which the refractive index was in exact agreement, to the fourth place, with literature values.

Furfural was purified by ordinary distillation in a metal pot still in 4-litre quantities, and distilled to give a very light yellow liquid product; 0·05 per cent triethylamine was added to the furfural as a polymerization inhibitor. The treated furfural was stored in dark Winchester bottles, and discoloration took place at a very slow rate. The colour change has no detectable influence on the purity, according to refractive index determinations, but any furfural which darkened appreciably was redistilled prior to use. Approximately 6 litres of each hydrocarbon and 12 litres of furfural were prepared thus.

TABLE I

Source and Final Purity of Materials Employed

Material	Source	B.p., °C		n_D^{20}		d_4^{20}	
		(Observed)	(Litt.)	(Observed)	(Litt.)	(Observed)	(Litt.)
Toluene	Staveley Coal and Iron Co. Ltd., Chesterfield, Derbyshire	110·6	(110·63)	1·4969	(1·49693)	0·8670	(0·86696)
Methyl*cyclo*hexane	Howards and Son Ltd., Ilford, Essex	100·9	(100·93)	1·4231	(1·42313)	0·7691	(0·76939)
n-Heptane	Phillips Petroleum Co., Oklahoma, U.S.A.	98·4	(98·43)	1·3878	(1·38765)	0·6850	(0·68368)
Furfural	Quaker Oats Co. Ltd., Southall, Middlesex	161·7	(161·7)	1·5261	(1·52608)	1·1590	(1·1598)

EXPERIMENTAL PROCEDURE

For binary mixtures, charges of 200 ml were prepared containing approximately 5, 10, 20, 30 . . . 80, 90, or 95 mol per cent of one component. Ternary mixtures were prepared in such a manner that the furfural content was held at a fixed value, whilst the ratio of the two hydrocarbons was varied. Five furfural concentration levels were used, and at each level five different hydrocarbon ratios were employed, giving 25 ternary runs in all.

The method of operation of the Fenske-type stills was similar to that described in the original paper on this still.[15] For the Gillespie still, a charge of 300 ml was employed, some liquid being withdrawn from the apparatus when the entire charge had reached boiling point, to compensate for the expansion which occurs. About 2½ to 3 hours were always allowed for equilibrium to be attained, and 10- to 20-ml samples of liquid and vapour condensate were withdrawn.

ANALYSIS

Methylcyclohexane–Toluene. Known mixtures of these two components were prepared, and their refractive index measured by a Pulfrich refractometer. The values obtained, together with previous data of Quiggle and Fenske,[35] are shown graphically in Fig 3, and excellent agreement exists between the two sets of data.

Toluene–Furfural. This binary mixture was analysed from refractive index data at 20° C. The results are plotted in Fig 4. No previous data existed for this system, and solutions were prepared and measured in an identical manner to the hydrocarbon

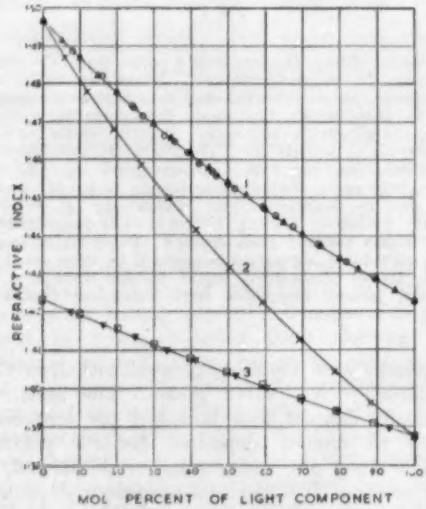

FIG 3

REFRACTIVE INDEX DATA FOR C_7 HYDROCARBON MIXTURES AT 20° C

Curve 1—Methyl*cyclo*hexane–toluene
Curve 2—*n*-heptane–toluene
Curve 3—*n*-heptane–methyl*cyclo*hexane

△ Quiggle and Fenske [35] ○ Garner and Hall
□ *F.I.A.T. Report* 1095 [16] ▽, × Bromiley and Quiggle [6]

binary above. An accuracy of between 0·10 and 0·15 per cent (mol) is to be expected from this procedure.

Methylcyclohexane–Furfural mixtures are nearly always two-phase at room temperature, but all concentrations become miscible above about 75° C. Hence the samples were first heated above the miscibility point, and a portion withdrawn and weighed. It was next washed with warm water (four times)—the furfural being extracted into the aqueous layer.

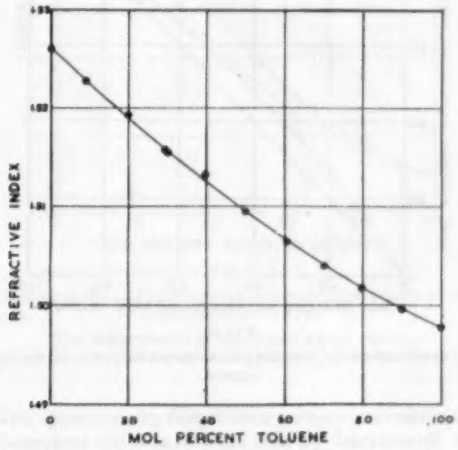

FIG 4

REFRACTIVE INDEX DATA FOR SYSTEM TOLUENE–FURFURAL AT 20° C

All washings were finally collected together, and analysed for furfural by the volumetric method of Hughes and Acree [24] employing a bromate–bromide mixture at 0° to 5° C.

Methylcyclohexane–Toluene–Furfural mixtures were analysed by a combined physical and chemical method. Furfural was first extracted by the above method and estimated. The hydrocarbon phase remaining in the separating flask was then given a sodium bisulphite wash to remove any traces of furfural, and a final water wash. The wet hydrocarbon phase was then dried overnight with clean metallic sodium, and analysed by refractive index.

RESULTS

Vapour pressure data for both hydrocarbons and furfural are summarized in Table II (together with data for normal heptane). Data for the hydrocarbons were obtained from the API Project No. 44 [1] tables, using Antoine equations to express the vapour pressure as a function of temperature. A few of the pressures fall outside the range of these equations, but the error of extrapolation is very small. The vapour pressure data for furfural in the literature were found to be inconsistent; [2, 13, 20, 37] all the data available were plotted as log p versus $10^3/T$. A mean curve was drawn through the points obtained, which corresponded to the equation:

$$\log p = (-2291/T) + 8{\cdot}1486 \quad . \quad (7)$$

This equation was further checked from the known value of the latent heat of vaporization and the Clapeyron–Clausius equation. Excellent agreement existed between the values of the constants obtained by the two methods.

TABLE II

Vapour Pressure Data

(1) Hydrocarbons

Source of Data: National Bureau Standards API Project No. 44. The vapour pressure is correlated by the Antoine equation:

$$\log_{10} p = A - \frac{B}{C + t}$$

or $$t = \frac{B}{A - \log_{10} p} - C$$

where p = vapour pressure, mm Hg;

t = °C.

Constants (for the range 500 to 1500 mm Hg).

Hydrocarbon	A	B	C
Toluene . . .	6·95334	1343·943	219·377
Methylcyclohexane .	6·82689	1272·864	221·630
n-Heptane . . .	6·90319	1268·586	216·954

(2) *Furfural*

From sources of data [2, 13, 20, 37] were plotted as log p *vs* $\frac{10^3}{T}$ and a mean curve drawn, which corresponded to the equation

$$\log p = -\frac{2291}{T} + 8{\cdot}1486$$

CALCULATION OF ACTIVITY COEFFICIENTS

To facilitate the calculation of true activity coefficients as distinct from overall correction factors, the deviation factors involved in the non-ideality of the vapour phase and pressure effects on the liquid were next calculated for each component involved. These vapour factors have been defined previously by equation (6), which becomes simplified for the case of atmospheric data to

$$\log z_1 = \frac{(p_1 - 760)(v_1 - B_1)}{2{\cdot}303\ RT} \quad . \quad (8)$$

The terms p_1, v_1, B_1 are all functions of temperature, and values of these were found at various temperatures between 100° and 160° C; consequently it was possible to express z_1 directly in terms of temperature. Table III summarizes z values for all components at 760 mm at a series of temperatures between 100° and 160° C. Values obtained by this method agree closely (within 1 per cent) with those using the recent nomograph of Scheibel.[36]

The method for calculating the virial coefficient was that of Wohl.[43]

$$B = \frac{RT_c}{P_c}\left(0{\cdot}197 - 0{\cdot}012T_r - \frac{0{\cdot}4}{T_r} - \frac{0{\cdot}146}{T_r^{3{\cdot}27}}\right) \quad (9)$$

Specific volumes for toluene and heptane were calculated from data in the International Critical Tables.[25] Values for methyl*cyclo*hexane were obtained by extrapolation of volumetric expansion coefficients.[10] Values for furfural were obtained from the *Quaker Oats Bulletin*.[34] Critical temperature and

TABLE III

z-Values for Hydrocarbons and Furfural

Temperature, °C	z-Values at 760 mm total pressure			
	Toluene	Methyl-*cyclo*-hexane	Heptane	Furfural
100	0·988	0·999	1·002	0·978
120	1·012	1·030	1·037	0·984
140	1·040	1·067	1·077	0·991
160	1·072	1·109	1·126	0·999

pressure values were available for all the hydrocarbons [10] with the exception of P_c for methyl*cyclo*hexane, which was calculated by the method of Meissner and Reading [29] using the critical volume, which itself is calculated from the parachor. A similar method was adopted for the furfural critical pressure. T_c for furfural was also calculated by methods of the same authors.[29]

Plots of the gas law deviation and liquid pressure factor z against temperature (at 760 mm pressure) are

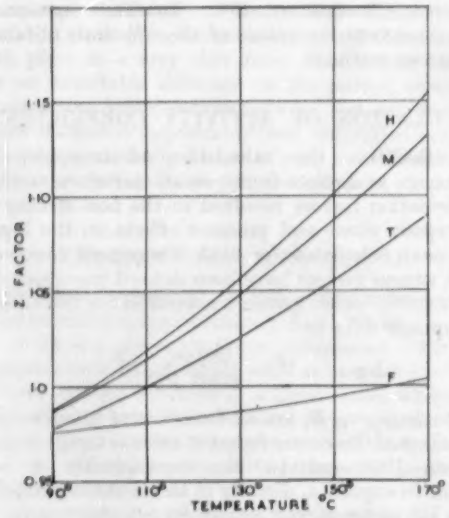

FIG 5

GAS CORRECTION FACTOR, z, AT 760 MM HG PRESSURE *vs* TEMPERATURE

given in Fig 5. In this way, the correction factor is available in a convenient and immediate form, thus introducing very little extra work into the calculation of true activity coefficient values.

BINARY SYSTEMS

(1) *Methyl*cyclo*hexane–Toluene*. This binary was investigated using a Fenske-type still, fitted with the simple non-jacketed sampling cup.

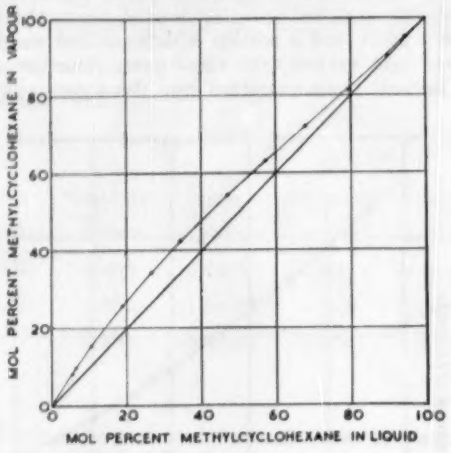

FIG 6

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE: EQUILIBRIUM CURVE

Equilibrium vapour and liquid phase compositions were determined (y_M and x_M) and also the temperature of the system. From these experimental data, other functions were derived, namely the relative volatility α_{expt}, and experimental activity coefficients for each component, labelled γ_M and γ_T respectively. These are defined as follows:

$$\alpha_{expt} = \frac{y_M/x_M}{y_T/x_T} \quad . \quad . \quad . \quad . \quad (10)$$

$$\gamma_M = \frac{\pi \cdot y_M}{p_M \cdot x_M} z_M \quad . \quad . \quad . \quad (11)$$

Figs 6, 7, 8, and 9 describe the equilibrium curve, temperature–composition curve, relative volatility–liquid composition curve, and activity coefficient curves for this system. For correlation purposes, a further function was calculated, namely $(T \log \gamma)^{-0.5}$ for each component, and this was plotted against the ratio of the liquid mol fractions, as in Fig 10. It is seen that this system is symmetrical, in that both components are represented by a single curve. The curves are drawn by the method of least squares, using weighted values of points lying in the most reliable region, *i.e.* where the mol ratio lies between 0·1 and 1·0. Below x–x ratios of 0·1, small errors in analysis become greatly magnified, and above 1·0 the experimental values of γ lie close to unity, causing $(T \log \gamma)^{-0.5}$ to become very large, and again subject to considerable error. This method of correlation is due to Li and Coull.[28] For component No. 1, their equation becomes:

$$(T \log \gamma_1)^{-0.5} = \left(\frac{b_1}{b_2}\right)\left(\frac{b_2}{k_{12}}\right)^{\frac{1}{4}}\left(\frac{x_1}{x_2}\right) + \left(\frac{b_2}{k_{12}}\right)^{\frac{1}{4}} \quad (12)$$

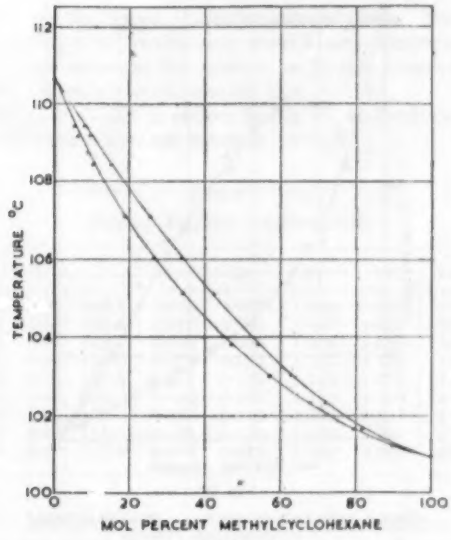

FIG 7

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE : TEMPERATURE–COMPOSITION CURVES

The lower curve is the liquid phase curve
The upper curve is the vapour phase curve

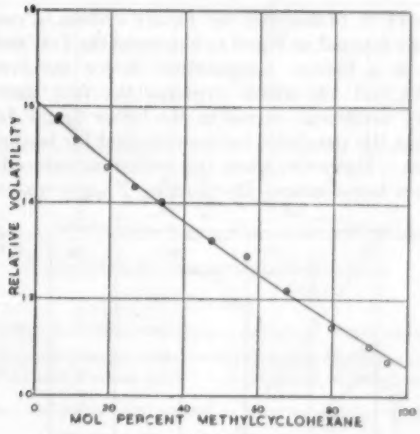

FIG 8

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE : RELATIVE VOLATILITY OF METHYL*CYCLO*HEXANE TO TOLUENE

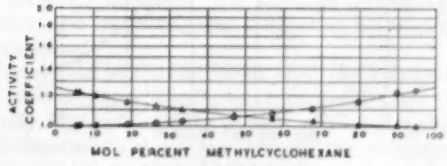

FIG 9

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE : ACTIVITY COEFFICIENTS

△ Methyl*cyclo*hexane ○ Toluene

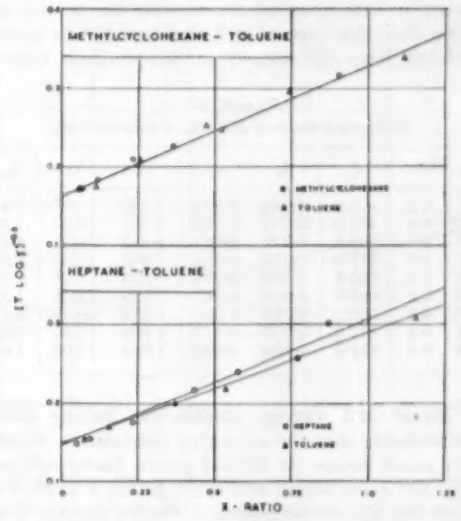

FIG 10

LI–COULL CORRELATION FOR SYSTEMS METHYL*CYCLO*HEXANE–TOLUENE AND HEPTANE–TOLUENE

Hence a plot of $(T \log \gamma_1)^{0.5}$ versus x_1/x_2 should give a straight line of slope

$$S_1 = \left(\frac{b_1}{b_2}\right)\left(\frac{b_2}{k_{12}}\right)^{\frac{1}{2}}$$

and an intercept

$$I_1 = \left(\frac{b_2}{k_{12}}\right)^{\frac{1}{2}} \text{ at } x_1/x_2 = 0$$

From the slope and intercept of the curve of Fig 10, the following correlations are derived. As this system is symmetrical, the denominations become unity.

$$T \log \gamma_M = 37{\cdot}19\, x_T^2 \quad . \quad . \quad (13)$$

$$T \log \gamma_T = 37{\cdot}19\, x_M^2 \quad . \quad . \quad (14)$$

Furthermore, the calculated relative volatility α_{calc} is expressed as

$$\alpha_{calc} = \frac{p_M \gamma_M x_T}{p_T \gamma_T x_M} \quad . \quad . \quad . \quad (15)$$

Another condition has to be satisfied, namely equation (4). By adjusting the temperature, trial and error solutions to the last equation can be made, to find the correct value of T and hence $t°$ C. Thus it is possible to obtain predicted values of t, γ_M and γ_T, α, y_M, and y_T from a given liquid composition. Such values are listed in Table IV, for values of x_M of 0·1, 0·2, . . . 0·9, 1·0. The curves drawn in Figs 6 to 9 are drawn from these calculated values, *i.e.* the curves represent predicted values rather than a line drawn to fit the experimental points only. In general, the agreement between the predicted curves and the experimental points appears to be quite satisfactory.

(2) *Toluene–Furfural.* Experimental determinations were initially carried out using a Fenske-type still with a vacuum-jacketed sampling cup. Sub-

sequent examination of the results led to the conclusion that this type of still was unsuited to systems involving large differences in temperature between

TABLE IV

Methylcyclohexane–Toluene Predicted Data

x_M	x_T	t	y_M	y_T	γ_M	γ_T	α_{calc}
0·1	0·9	108·6	0·146	0·854	1·199	1·002	1·54
0·2	0·8	106·9	0·270	0·730	1·154	1·009	1·48
0·3	0·7	105·6	0·379	0·621	1·117	1·021	1·42
0·4	0·6	104·5	0·476	0·524	1·085	1·037	1·36
0·5	0·5	103·6	0·566	0·434	1·058	1·058	1·305
0·6	0·4	102·8	0·655	0·345	1·037	1·085	1·26
0·7	0·3	102·2	0·736	0·264	1·021	1·118	1·195
0·8	0·2	101·6	0·823	0·177	1·009	1·157	1·16
0·9	0·1	101·2	0·908	0·092	1·002	1·203	1·09

the liquid and vapour condensate boiling points. It is probable that the returning condensate, which is never much below its boiling point, flashes off as it enters the main liquid reservoir, giving a vapour too rich in the lighter component. Such a process would

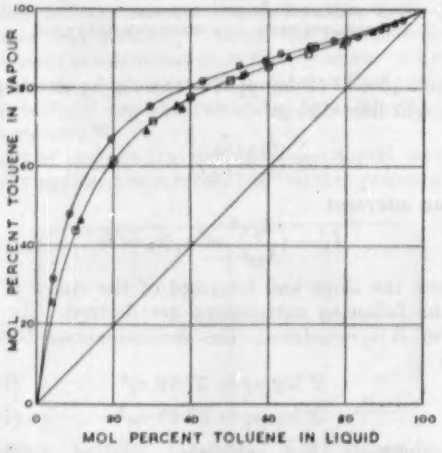

FIG 11

SYSTEM TOLUENE–FURFURAL: EQUILIBRIUM DIAGRAM

○ Experimental determination—Fenske still
△ ,, ,, —Gillespie still
⊡ Values calculated by equations (16) and (17)

tend to perpetuate itself. The results on the Fenske still were consistent in themselves, but failed to comply with a test of true equilibrium developed later in this paper. Consequently the system was re-examined using a modified Gillespie still, where the two phases separate in an adiabatic disengaging chamber, and recombine only after cooling to a low temperature. The results satisfied much more exactly the criteria of equilibrium demanded by the Li–Coull method. The Li–Coull equations describing the system are:

$$T \log \gamma_T = \frac{162{\cdot}8\ x_F^2}{(x_T + 1{\cdot}094\ x_F)^2} \quad . \quad (16)$$

$$T \log \gamma_F = \frac{123{\cdot}8\ x_T^2}{(x_F + 0{\cdot}914\ x_T)^2} \quad . \quad (17)$$

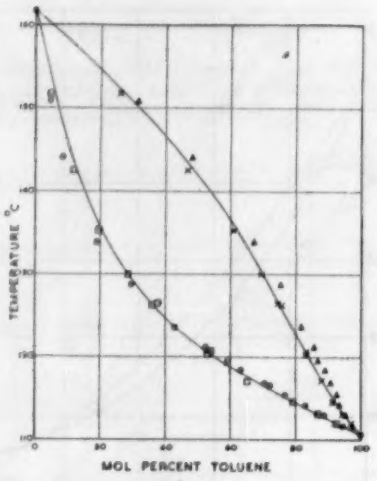

FIG 12

SYSTEM TOLUENE–FURFURAL: TEMPERATURE–COMPOSITION CURVES

○ Experimental determinations—liquid phase—Fenske still
△ ,, ,, —vapour phase— ,,
⊡ ,, ,, —liquid phase—Gillespie still
× ,, ,, —vapour phase— ,,

The solid curves are derived from equations (16) and (17).

Figs 11 to 14 describe the binary system in exactly the same manner as Figs 6 to 9 covered the first system. There is a hidden temperature factor involved in Figs 13 and 14, which explains the fact that the activity coefficient curves in the latter figure do not resemble the parabolic curves obtained for isothermal systems. However, when the system is reduced to a common temperature, *i.e.* plotting $T \log \gamma$ instead of

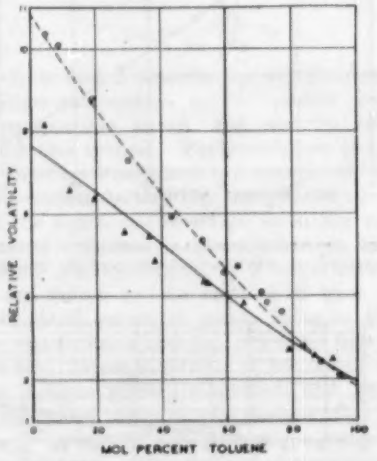

FIG 13

SYSTEM TOLUENE–FURFURAL: RELATIVE VOLATILITY OF TOLUENE TO FURFURAL

○ Fenske still determinations
△ Gillespie still determinations

γ, the normal types of curves are obtained. Such a divergence is noticeable only when a large temperature variation occurs in the system, as in this case where there is a variation of some 50° C.

A Li–Coull plot is shown in Fig 15, and calculated equilibrium values are listed in Table V.

TABLE V

Toluene–Furfural Predicted Data

x_T	x_F	t	y_T	y_F	γ_T	γ_F	α_{calc}
0·1	0·9	146·1	0·441	0·559	1·854	1·007	7·09
0·2	0·8	135·4	0·619	0·381	1·662	1·030	6·51
0·3	0·7	129·1	0·717	0·283	1·494	1·069	5·92
0·4	0·6	124·6	0·778	0·222	1·354	1·130	5·27
0·5	0·5	121·3	0·821	0·179	1·242	1·218	4·60
0·6	0·4	118·7	0·856	0·144	1·152	1·339	3·98
0·7	0·3	116·5	0·888	0·112	1·085	1·501	3·42
0·8	0·2	114·5	0·921	0·079	1·038	1·720	2·90
0·9	0·1	112·6	0·956	0·044	1·009	2·020	2·42

(3) *Methylcyclohexane–Furfural.* This system is even less ideal than the previous one, and exhibits partial miscibility at room temperature. The system

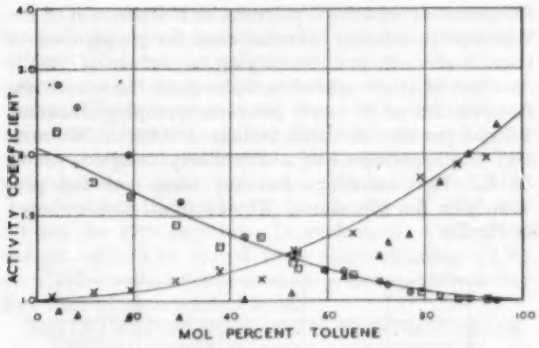

FIG 14

SYSTEM TOLUENE–FURFURAL : ACTIVITY COEFFICIENTS

○ Toluene (Fenske still) ⊡ Toluene (Gillespie still)
△ Furfural (Fenske still) × Furfural (Gillespie still)

The solid curves correspond to equations (16) and (17).

is, however, entirely miscible at its atmospheric boiling point. Physical analysis becomes impossible with two liquid phases present, and chemical analysis was adopted involving the aqueous extraction of furfural, and its subsequent estimation by controlled bromination.

This system was investigated using the Fenske-type still with a vacuum-jacketed condensate cup. The severely non-ideal nature of this system is reflected in the unusual nature of the temperature–composition curve (Fig 17), in that it is virtually isothermal over 80 per cent of the entire concentration range. Hence the "flashing" effect observed in the toluene–furfural system is absent except for the range 0 to 10 per cent

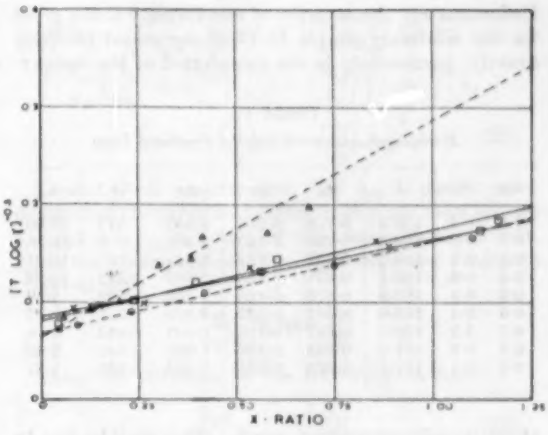

FIG 15

SYSTEM TOLUENE–FURFURAL : LI-COULL CORRELATION

○ Toluene (Fenske still) ⊡ Toluene (Gillespie still)
△ Furfural (Fenske still) × Furfural (Gillespie still)

naphthene, which would play a minor rôle in correlation due to the effect of small analytical errors in this range. The correlating Li–Coull equations for this system are :

$$T \log \gamma_M = \frac{349{\cdot}8\ x_F^2}{(x_M + 1{\cdot}050\ x_F)^2} \quad . \quad (18)$$

$$T \log \gamma_F = \frac{303{\cdot}6\ x_M^2}{(x_F + 0{\cdot}952\ x_M)^2} \quad . \quad (19)$$

and calculated equilibrium values are listed in Table VI.

The corresponding curves appear in Figs 16 to 19.

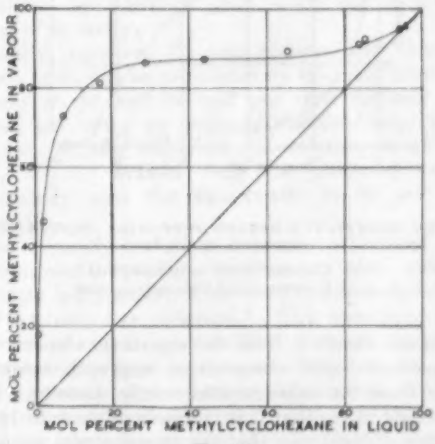

FIG 16

SYSTEM METHYL*CYCLO*HEXANE–FURFURAL : EQUILIBRIUM DIAGRAM

○ Experimental determinations
△ Azeotrope

The solid curve is derived from equations (18) and (19).

Unfortunately the severity of non-ideality is too great for the relatively simple Li–Coull [illegible]stions to apply exactly, particularly in the calculation of the temper-

TABLE VI

Methylcyclohexane–Furfural Predicted Data

x_M	x_F	t	y_M	y_F	γ_M	γ_F	α_{calc}
0·1	0·9	120·3	0·742	0·258	4·562	1·017	25·90
0·2	0·8	108·4	0·850	0·150	3·485	1·076	24·04
0·3	0·7	104·3	0·866	0·134	2·645	1·187	15·91
0·4	0·6	103·1	0·874	0·126	2·065	1·362	10·94
0·5	0·5	102·9	0·875	0·125	1·663	1·628	7·02
0·6	0·4	102·8	0·877	0·123	1·390	2·034	4·72
0·7	0·3	102·5	0·881	0·119	1·207	2·660	3·16
0·8	0·2	101·9	0·894	0·106	1·087	3·640	2·09
0·9	0·1	101·1	0·925	0·075	1·022	5·223	1·37

ature–liquid composition curve. This may be due to one of two causes:

(*a*) The relation $(T \log \gamma)_{x_1 x_2} =$ constant may not apply exactly over a temperature range of sixty degrees.

(*b*) The Li–Coull expressions are themselves too simple to describe the system.

The divergence is not great, however, and the activity coefficient, equilibrium and relative volatility

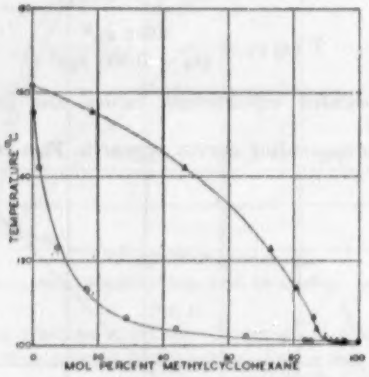

FIG 17

SYSTEM METHYL*CYCLO*HEXANE–FURFURAL: TEMPERATURE COMPOSITION CURVES

○ Experimental values (liquid)
△ Experimental values (vapour)

curves are obtained from the equations above. The temperature–liquid composition curve, however, is drawn from the experimental results directly. It is interesting to see that it is precisely in the 0 to 10 per cent naphthene range that the experimental values of γ show a marked divergence from the correlated curve; this is attributed to flashing in the still.

The relative volatility curve indicated that an azeotrope existed at approximately 95 mol per cent methyl*cyclo*hexane. This was confirmed by the

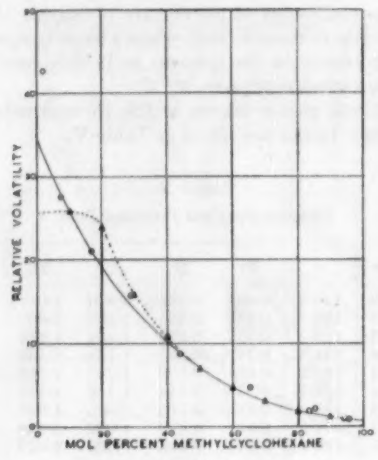

FIG 18

SYSTEM METHYL*CYCLO*HEXANE–FURFURAL: RELATIVE VOLATILITY OF METHYL*CYCLO*HEXANE TO FURFURAL

○ Experimental determinations
△ Calculated from equations (18) and (19)

fractionation of a 95–5 per cent mixture in one of the thirty-plate refining columns used for preparation of pure materials and employing a reflux of 25 : 1. Analysis of six overhead samples gave the azeotropic composition as 95·8 mol per cent methyl*cyclo*hexane, 4·2 mol per cent furfural, boiling at 100·8° C/760 mm, and the azeotrope has a miscibility temperature of 16° C. This azeotrope has not been recorded previously in the literature. The Li–Coull plot is shown in Fig 20.

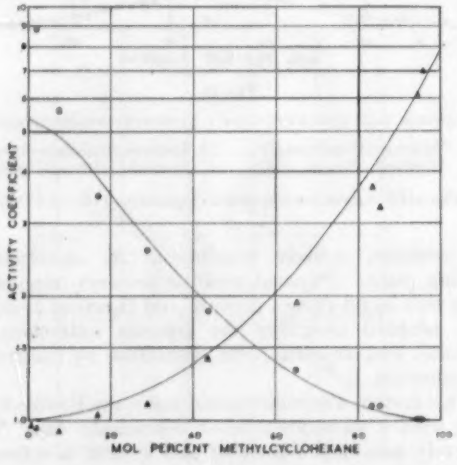

FIG 19

SYSTEM METHYL*CYCLO*HEXANE–FURFURAL: ACTIVITY COEFFICIENTS

○ Methyl*cyclo*hexane △ Furfural

The solid curves are derived from equations (18) and (19).

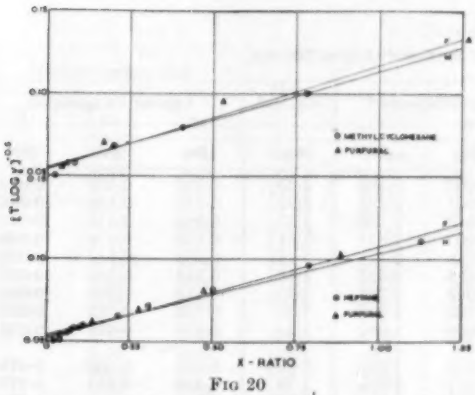

FIG 20

LI–COULL CORRELATIONS FOR SYSTEMS METHYL*CYCLO*-HEXANE–FURFURAL AND HEPTANE–FURFURAL

THE TERNARY SYSTEM METHYL*CYCLO*-HEXANE–TOLUENE–FURFURAL

Experimental Data. All experimental work was carried out on the Fenske type of still, mostly using a vacuum-jacketed sample cup.

The introduction of a further concentration variable makes a graphical presentation of experimental results difficult, and subject to much interpolation. Hence activity coefficients and relative volatilities were obtained from experimental data, and each derived function compared numerically with the predicted values obtained from the Li–Coull equations as extended to ternary systems. Five series of runs were made at approximately 15, 30, 45, 65, and 80 mol per cent furfural. In each series, the hydrocarbon ratio was varied from approximately 17/83 to 83/17 (methyl*cyclo*hexane to toluene), there being five runs at each solvent level.

The Li–Coull ternary equations [28] are based entirely on constants derived from the participating binary systems. The effect of ternary collisions is therefore ignored, but it is unlikely to play an important rôle in determining the activities of the various molecular species.

For each component in turn :

$$T \log \gamma_1 = \left\{\left(\frac{k_{12}}{b_1}\right)\left(\frac{b_2}{b_1}\right) x_2^2 + \left(\frac{k_{13}}{b_1}\right)\left(\frac{b_3}{b_1}\right) x_3^2 + \left[\left(\frac{k_{12}}{b_1}\right)\left(\frac{b_3}{b_1}\right) + \left(\frac{k_{13}}{b_1}\right)\left(\frac{b_2}{b_1}\right) - \left(\frac{k_{23}}{b_1}\right)\right] x_2 x_3\right\} \Big/ \left\{x_1 + \left(\frac{b_2}{b_1}\right) x_2 + \left(\frac{b_3}{b_1}\right) x_3\right\}^2 \quad . \quad . \quad (20)$$

$$T \log \gamma_2 = \left\{\left(\frac{k_{12}}{b_2}\right)\left(\frac{b_1}{b_2}\right) x_1^2 + \left(\frac{k_{23}}{b_2}\right)\left(\frac{b_3}{b_2}\right) x_3^2 + \left[\left(\frac{k_{12}}{b_2}\right)\left(\frac{b_3}{b_2}\right) + \left(\frac{k_{23}}{b_2}\right)\left(\frac{b_1}{b_2}\right) - \left(\frac{k_{13}}{b_2}\right)\right] x_1 x_3\right\} \Big/ \left\{x_2 + \left(\frac{b_1}{b_2}\right) x_1 + \left(\frac{b_3}{b_2}\right) x_3\right\}^2 \quad . \quad . \quad (21)$$

$$T \log \gamma_3 = \left\{\left(\frac{k_{13}}{b_3}\right)\left(\frac{b_1}{b_3}\right) x_1^2 + \left(\frac{k_{23}}{b_3}\right)\left(\frac{b_2}{b_3}\right) x_2^2 + \left[\left(\frac{k_{13}}{b_3}\right)\left(\frac{b_2}{b_3}\right) + \left(\frac{k_{23}}{b_3}\right)\left(\frac{b_1}{b_3}\right) - \left(\frac{k_{12}}{b_3}\right)\right] x_1 x_2\right\} \Big/ \left\{x_3 + \left(\frac{b_1}{b_3}\right) x_1 + \left(\frac{b_2}{b_3}\right) x_2\right\}^2 \quad . \quad . \quad (22)$$

Li and Coull assume also that k_{12} is nearly independent of the presence of molecules other than species 1 and 2, *i.e.* k_{12} in a ternary mixture is identical with k_{12} in the binary system 1–2. The only new constants involved are :

$$\frac{k_{23}}{b_1},\ \frac{k_{13}}{b_2},\ \text{and}\ \frac{k_{12}}{b_3}$$

These are obtained by the following method :

$$\frac{k_{12}}{b_3} = \frac{(k_{12}/b_1)_{12}}{(b_3/b_1)_{13}} \quad . \quad . \quad . \quad (23)$$

$$\frac{k_{13}}{b_2} = \frac{(k_{13}/b_1)_{13}}{(b_2/b_1)_{12}} \quad . \quad . \quad . \quad (24)$$

$$\frac{k_{23}}{b_1} = \frac{(k_{23}/b_2)_{23}}{(b_1/b_2)_{12}} \quad . \quad . \quad . \quad (25)$$

i.e. ternary correlation by this method involves no data other than those of the constituent binary data. It is found that in all the ternary systems examined, equation (26), which is a necessary restriction imposed by the previous equations, holds to a very close degree—within the limits of experimental errors :

$$\left(\frac{b_1}{b_2}\right)_{12} = \frac{(b_1/b_3)_{13}}{(b_2/b_3)_{23}} \quad . \quad . \quad . \quad (26)$$

From the equations presented, it is possible to predict values of γ_1, γ_2, and γ_3; furthermore, the relative volatility of the hydrocarbon components may be calculated by equation (15), using the calculated values of γ_1 and γ_2.

Finally, equation (3) also applies, and thus the boiling point can be calculated by trial and error.

Runs at 15 and 30 mol per cent furfural were carried out using an ordinary distillate cup, which resulted in the experimental relative volatilities being slightly greater than the predicted values, particularly with the runs made at 30 per cent furfural.

The overall deviation between calculated and experimental activity coefficients and relative volatility is 2 per cent, if two results are excluded out of the twenty-five obtained.* This compares quite favourably with other published data on analogous systems. The poor agreement found in the two rejected sets is due to errors inherent in analysis, which occur only when a high toluene concentration is involved; there is a tendency for the toluene to retain some of the furfural at the extraction stage, even after three or four extractions.

The experimental results are correlated by the

* As in other parts of this paper, only correlated equilibrium data are quoted, in order to conserve space. Experimental data are obtainable, in the form of photostat copies, from the Chemical Engineering Department, Birmingham University.

TABLE VII

Methylcyclohexane–Toluene–Furfural Predicted Data at 760 mm

Liquid composition.			B.p., t° C	y_M*	Activity coefficients			Rel. vol.	Vapour composition		
x_F	x_M	x_T			γ_M	γ_T	γ_F	α_{MT}	y_M	y_T	y_F
0·10	0·09	0·81	110·3	0·158	1·314	1·003	2·189	1·69	0·151	0·805	0·044
	0·18	0·72	108·5	0·289	1·262	1·001	2·375	1·63	0·276	0·680	0·044
	0·27	0·63	106·9	0·402	1·214	1·002	2·590	1·57	0·384	0·571	0·045
	0·36	0·54	105·7	0·502	1·171	1·007	2·833	1·51	0·478	0·474	0·048
	0·45	0·45	104·7	0·593	1·135	1·016	3·113	1·46	0·563	0·387	0·050
	0·54	0·36	103·8	0·678	1·104	1·028	3·426	1·40	0·642	0·305	0·053
	0·63	0·27	102·9	0·759	1·076	1·046	3·786	1·35	0·715	0·228	0·057
	0·72	0·18	102·3	0·839	1·054	1·065	4·203	1·30	0·786	0·152	0·062
	0·81	0·09	101·6	0·918	1·035	1·090	4·660	1·25	0·854	0·076	0·070
0·20	0·08	0·72	112·0	0·169	1·468	1·025	1·830	1·835	0·156	0·766	0·078
	0·16	0·64	110·0	0·308	1·405	1·017	1·953	1·78	0·284	0·639	0·077
	0·24	0·56	108·3	0·425	1·350	1·009	2·092	1·725	0·392	0·530	0·078
	0·32	0·48	106·9	0·527	1·298	1·007	2·245	1·67	0·485	0·436	0·079
	0·40	0·40	105·7	0·618	1·253	1·006	2·415	1·62	0·568	0·351	0·081
	0·48	0·32	104·7	0·700	1·212	1·008	2·608	1·565	0·642	0·273	0·085
	0·56	0·24	103·8	0·778	1·174	1·013	2·822	1·515	0·710	0·201	0·089
	0·64	0·16	103·1	0·855	1·142	1·020	3·065	1·465	0·774	0·132	0·094
	0·72	0·08	102·5	0·928	1·113	1·030	3·335	1·415	0·835	0·065	0·100
0·30	0·07	0·63	113·8	0·180	1·666	1·069	1·572	1·985	0·161	0·732	0·107
	0·14	0·56	111·5	0·327	1·598	1·054	1·653	1·945	0·293	0·603	0·104
	0·21	0·49	109·6	0·448	1·533	1·042	1·740	1·890	0·402	0·496	0·102
	0·28	0·42	108·0	0·552	1·474	1·031	1·835	1·845	0·496	0·403	0·101
	0·35	0·35	106·7	0·643	1·419	1·024	1·942	1·795	0·577	0·321	0·102
	0·42	0·28	105·6	0·724	1·369	1·018	2·059	1·745	0·648	0·248	0·104
	0·49	0·21	104·6	0·799	1·321	1·015	2·186	1·695	0·712	0·181	0·107
	0·56	0·14	103·9	0·868	1·279	1·013	2·326	1·645	0·773	0·117	0·110
	0·63	0·07	103·1	0·936	1·241	1·014	2·484	1·600	0·828	0·057	0·115
0·40	0·06	0·54	115·6	0·194	1·925	1·133	1·385	2·155	0·168	0·698	0·134
	0·12	0·48	113·1	0·346	1·852	1·114	1·435	2·125	0·303	0·571	0·126
	0·18	0·42	110·9	0·471	1·780	1·098	1·489	2·085	0·414	0·464	0·122
	0·24	0·36	109·1	0·527	1·713	1·083	1·550	2·040	0·507	0·374	0·119
	0·30	0·30	107·6	0·666	1·649	1·070	1·614	1·990	0·588	0·295	0·117
	0·36	0·24	106·3	0·745	1·590	1·059	1·686	1·945	0·658	0·225	0·117
	0·42	0·18	105·2	0·817	1·536	1·049	1·763	1·905	0·721	0·162	0·117
	0·48	0·12	104·2	0·882	1·484	1·040	1·846	1·860	0·777	0·104	0·119
	0·54	0·06	103·4	0·942	1·435	1·034	1·936	1·815	0·827	0·051	0·122
0·50	0·05	0·45	117·8	0·206	2·256	1·221	1·248	2·335	0·173	0·665	0·162
	0·10	0·40	114·9	0·366	2·182	1·201	1·279	2·315	0·311	0·538	0·151
	0·15	0·35	112·4	0·495	2·107	1·182	1·312	2·28	0·425	0·433	0·142
	0·20	0·30	110·3	0·600	2·035	1·164	1·348	2·245	0·520	0·346	0·134
	0·25	0·25	108·6	0·689	1·964	1·148	1·339	2·21	0·599	0·271	0·130
	0·30	0·20	107·0	0·764	1·899	1·132	1·429	2·17	0·668	0·205	0·127
	0·35	0·15	105·6	0·854	1·834	1·118	1·472	2·13	0·730	0·146	0·124
	0·40	0·10	104·7	0·894	1·775	1·105	1·522	2·09	0·782	0·094	0·124
	0·45	0·05	103·9	0·950	1·709	1·092	1·574	2·04	0·830	0·045	0·125
0·60	0·04	0·36	120·7	0·218	2·680	1·336	1·148	2·515	0·175	0·627	0·198
	0·08	0·32	117·4	0·386	2·611	1·315	1·166	2·515	0·317	0·504	0·179
	0·12	0·28	114·6	0·517	2·538	1·296	1·186	2·490	0·431	0·404	0·165
	0·16	0·24	112·3	0·623	2·467	1·277	1·206	2·475	0·527	0·319	0·154
	0·20	0·20	110·1	0·710	2·394	1·260	1·228	2·445	0·606	0·248	0·146
	0·24	0·16	108·3	0·785	2·327	1·242	1·252	2·415	0·675	0·186	0·139
	0·28	0·12	106·7	0·848	2·257	1·226	1·277	2·385	0·734	0·132	0·134
	0·32	0·08	105·3	0·904	2·190	1·209	1·304	2·355	0·786	0·083	0·131
	0·36	0·04	104·1	0·953	2·128	1·193	1·331	2·325	0·833	0·040	0·127
0·70	0·03	0·27	124·8	0·232	3·215	1·479	1·078	2·705	0·174	0·578	0·248
	0·06	0·24	121·2	0·404	3·148	1·462	1·086	2·70	0·313	0·464	0·223
	0·09	0·21	118·1	0·536	3·091	1·445	1·100	2·705	0·429	0·370	0·201
	0·12	0·18	115·3	0·643	3·031	1·427	1·109	2·70	0·524	0·291	0·185
	0·15	0·15	112·8	0·728	2·971	1·410	1·120	2·63	0·605	0·224	0·171
	0·18	0·12	110·7	0·801	2·907	1·393	1·130	2·68	0·673	0·167	0·160
	0·21	0·09	108·8	0·862	2·842	1·376	1·145	2·665	0·731	0·117	0·152
	0·24	0·06	107·1	0·914	2·775	1·360	1·158	2·64	0·782	0·074	0·144
	0·27	0·03	105·6	0·960	2·713	1·344	1·171	2·62	0·825	0·036	0·139

y_M* = solvent-free mol fraction of M.

TABLE VII—*continued*

Liquid composition			B.p., t° C	y_M*	Activity coefficients			Rel. vol.	Vapour composition		
x_F	x_M	x_T			γ_M	γ_T	γ_F	α_{MT}	y_M	y_T	y_F
0·80	0·02	0·18	131·3	0·242	3·874	1·652	1·033	2·885	0·161	0·504	0·335
	0·04	0·16	127·5	0·421	3·844	1·645	1·038	2·90	0·295	0·406	0·299
	0·06	0·14	124·2	0·555	3·807	1·630	1·041	2·92	0·407	0·325	0·268
	0·08	0·12	121·2	0·660	3·766	1·617	1·046	2·935	0·500	0·256	0·244
	0·10	0·10	118·4	0·746	3·728	1·605	1·050	2·94	0·580	0·197	0·223
	0·12	0·08	115·9	0·815	3·689	1·593	1·055	2·945	0·648	0·147	0·205
	0·14	0·06	113·7	0·873	3·639	1·580	1·060	2·935	0·706	0·103	0·191
	0·16	0·04	111·7	0·922	3·588	1·567	1·066	2·935	0·756	0·064	0·180
	0·18	0·02	109·9	0·964	3·534	1·552	1·071	2·93	0·801	0·030	0·169
0·90	0·01	0·09	142·3	0·250	4·615	1·849	1·007	3·005	0·120	0·361	0·519
	0·02	0·08	139·1	0·424	4·618	1·847	1·008	3·025	0·226	0·307	0·467
	0·03	0·07	136·2	0·558	4·623	1·844	1·009	3·05	0·318	0·252	0·430
	0·04	0·06	133·6	0·671	4·619	1·841	1·010	3·07	0·404	0·198	0·398
	0·05	0·05	131·0	0·755	4·615	1·837	1·012	3·09	0·478	0·154	0·368
	0·06	0·04	128·6	0·823	4·609	1·832	1·013	3·105	0·544	0·116	0·340
	0·07	0·03	126·4	0·880	4·597	1·828	1·014	3·12	0·601	0·082	0·317
	0·08	0·02	124·3	0·926	4·585	1·823	1·015	3·135	0·653	0·052	0·295
	0·09	0·01	122·3	0·965	4·572	1·817	1·016	3·15	0·699	0·025	0·276
1·00	0·00	0·00	161·7	0·000	5·359	2·055	1·000	3·030	0·000	0·000	1·000

y_M* = solvent-free mol fraction of M.

following equations, based exclusively upon data obtained from the constituent binary systems :

$$T \log \gamma_M = \frac{37{\cdot}19x_T^2 + 349{\cdot}8x_F^2 + 223{\cdot}3x_Tx_F}{(x_M + x_T + 1{\cdot}050x_F)^2} \quad (27)$$

$$T \log \gamma_T = \frac{37{\cdot}19x_M^2 + 162{\cdot}8x_F^2 - 143{\cdot}6x_Mx_F}{(x_T + x_M + 1{\cdot}094x_F)^2} \quad (28)$$

$$T \log \gamma_F = \frac{303{\cdot}6x_M^2 + 123{\cdot}8x_T^2 + 385{\cdot}1x_Mx_T}{(x_F + 0{\cdot}952x_M + 0{\cdot}914x_T)^2} \quad (29)$$

PREDICTED DATA ON TERNARY SYSTEMS SUITABLE FOR GRAPHICAL PRESENTATION

To make full use of the correlating equations, and to obtain data in a form suitable for graphical interpretation, such as can be used in extractive distillation calculations, complete sets of predicted data have been prepared in Table VII for the ternary system. The values were obtained with the aid of a " Marchant " automatic electric calculating machine. The general procedure was as follows :

(1) The mol fraction of furfural was fixed at definite intervals of 0·1, from 0·0 to 1·0.

(2) At each furfural level eleven hydrocarbon compositions corresponding to solvent-free concentrations of 0, 10, 20, . . . 90, and 100 per cent were then fixed.

(3) Using the correlating equations developed (20) to (22), the values of $T \log \gamma$ for each component were obtained.

(4) By interpolation of experimental results, approximate values of the temperature t and hence T were obtained, and provisional solutions for γ_1, γ_2, and γ_3 developed.

(5) At the provisional temperature t, values for p_1, p_2, and p_3 were obtained and similarly z_1, z_2, and z_3.

(6) Hence the total pressure π is calculated as $\sum_{123} \frac{p\gamma x}{z}$.

(7) If this result differed appreciably from 760 mm, a new temperature t was fixed, and new solutions made for the γ, p, and z values. Normally a second trial sufficed.

(8) Once the final temperature had been established, values of the relative volatility of the hydrocarbons α_{MT} were evaluated by equation (15).

(9) Values of the equilibrium vapour composition were then deduced by the relation

$$y_i = \frac{p_i\gamma_ix_i}{z_i}\Big/\pi \quad . \quad . \quad . \quad (30)$$

(10) Finally, in order to obtain equilibrium curves at fixed solvent concentrations, the solvent-free hydrocarbon compositions y^* were determined.

All the above values have been expressed graphically in Figs 21 to 26, which represent respectively :

Boiling point *versus* liquid hydrocarbon composition (parameter–per cent furfural).

Relative volatility *versus* hydrocarbon composition (parameter–per cent furfural).

Methyl*cyclo*hexane activity coefficient *versus* hydrocarbon composition (parameter–per cent furfural).

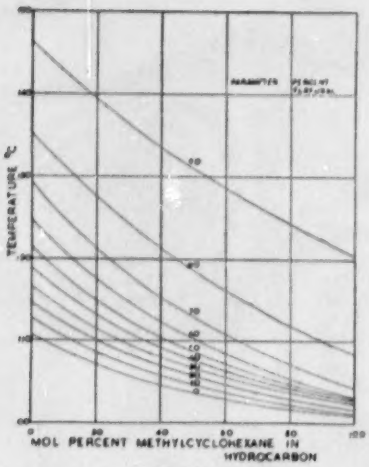

FIG 21

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE–FURFURAL: TEMPERATURE–COMPOSITION CURVES

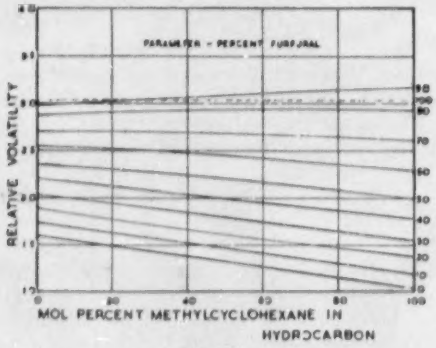

FIG 22

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE–FURFURAL: RELATIVE VOLATILITY OF METHYL*CYCLO*HEXANE TO TOLUENE IN THE PRESENCE OF FURFURAL

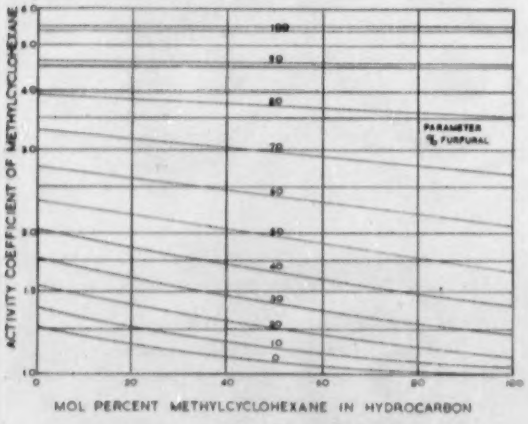

FIG 23

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE–FURFURAL: ACTIVITY COEFFICIENT OF METHYL*CYCLO*HEXANE

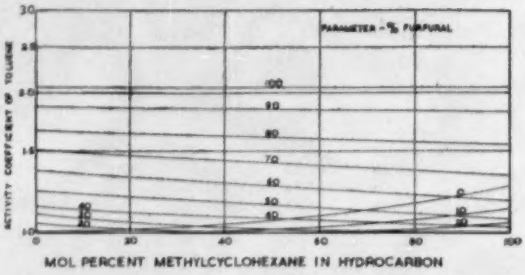

FIG 24

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE–FURFURAL: ACTIVITY COEFFICIENT OF TOLUENE

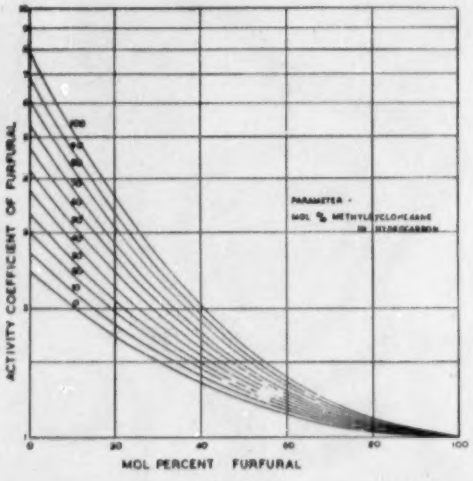

FIG 25

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE–FURFURAL: ACTIVITY COEFFICIENT OF FURFURAL

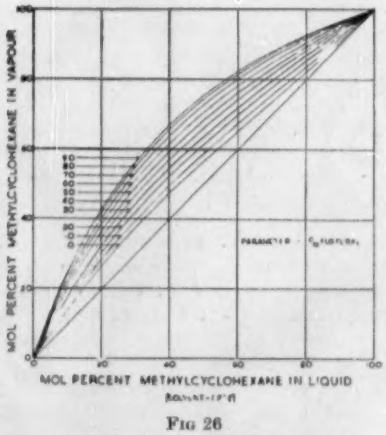

FIG 26

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE–FURFURAL: EFFECT OF FURFURAL ON THE VAPOUR–LIQUID EQUILIBRIUM CURVE OF THE HYDROCARBON BINARY

Toluene activity coefficient *versus* hydrocarbon composition (parameter–per cent furfural).
Furfural activity coefficient *versus* furfural composition (parameter–hydrocarbon composition).
Equilibrium curve for the hydrocarbons (parameter–per cent furfural).

The behaviour of the ternary system is depicted clearly in this manner, and several interesting characteristics have been found, particularly that the relative volatility increases with increased solvent concentration, but only up to a point. At very high furfural concentrations α actually falls, and this may be important in the selection of operating conditions in an extractive distillation unit, particularly when the solvent boils at a much higher temperature than the key components, and when the systems are more ideal than in the case under consideration. This behaviour confirms the theoretical deductions of Herington.[23]

TERNARY ANALYTICAL DATA

When it was realized that chemical analysis of certain ternary mixtures rich in toluene was unreliable, it was decided to obtain complete sets of

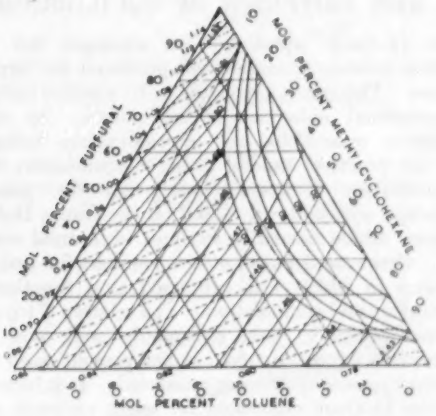

FIG 27

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE–FURFURAL: ANALYTICAL DIAGRAM

The solid lines represent lines of constant refractive index (n_D^{20}).
The broken lines represent lines of constant density (ρ_4^{20}).
The solid curves represent curves of constant miscibility temperature (° C).

analytical data for the ternary system. The method used was similar to that of Carlson, Schubert, and Fenske.[7] Using ten different hydrocarbon ratios at fixed furfural concentrations of 0, 10, 20, . . . 90, and 100 per cent about 100 samples were prepared, of known composition by weight. These mixtures were prepared volumetrically using 0- to 10-ml burettes and 0- to 1-ml pipettes, weighings being made after each operation. Compositions were finally expressed as mol percentages. In the case of mixtures miscible at 20° C, the refractive index and specific gravity values were determined by Pulfrich refractometer and modified Westphal balance respectively, the samples required being 1 ml and 20 to 25 ml. Two-phase mixtures were placed in the Westphal balance cylinder, and the circulating water heated until the cloud point or critical solution temperature was reached. Measurements were made at both disappearance and reappearance of the second phase. Values obtained are presented graphically in Fig 27.

DISCUSSION

Pressure measurements were accurate to ± 1 mm, corresponding to a temperature variation of 0·05° C. Temperature measurements were, however, accurate only to 0·20° C, and a more sensitive instrument would have been desirable. Inherent failure of still operation, due to the still design must be considered. Very few absolute criteria exist for thermodynamic equilibrium,[21] but it is believed that the Li–Coull method of correlation offers a possible criterion, particularly for isobaric systems, which are discussed below.

It is likely that the Fenske still, in common with most stills employing a recirculation principle, tends to exhibit "flashing" of returning condensate, when the difference in boiling point between liquid charge and condensate is more than about 10° C. It is interesting to see from Figs 13 and 18 that the experimental relative volatility values always lie above the correlation curve, where such differences in temperature exist, and furthermore, the greater the temperature difference, the greater the discrepancy. It is therefore concluded that the Fenske still is eminently suitable for both ideal and non-ideal solutions whenever the liquid and condensate boil within 10° to 20° C of each other, but tends to exhibit fractionation effects outside these conditions. Other investigators have since confirmed this conclusion.[40] In such cases the Gillespie still, as modified according to previous details, gives more reliable results.

It is also apparent that physical methods of analysis of ternary mixtures are preferable to chemical methods, which, however, should be employed when two phases are present. For the experimental runs, made at 15 per cent furfural, the hydrocarbon phase remaining after furfural extraction was sufficiently large to result in a water–hydrocarbon ratio in the extraction process of only 5 : 1, whereas in the runs, at 80 per cent furfural, the ratio would be 80 : 1, ensuring complete extraction of the polar compound. A ratio of 5 : 1 proved satisfactory, however, when the toluene content of the hydrocarbon phase was small. However, the chemical analysis of some samples taken from runs at 15 per cent furfural concentration was in error for this reason. The subsequent hydrocarbon analysis is correct, however, as the material was given a bisulphite wash prior to analysis.

Hence the relative volatility values (experimental and predicted) agreed in these cases more closely than the activity coefficient values.

The average deviation for all ternary data was about 3·5 per cent, and the overall averages of experimental and predicted values of γ and α agreed within 0·5 per cent, indicating that no particular functions were consistently lower or higher than the calculated values.

APPLICABILITY OF THE LI–COULL METHOD

The use of z-factors in the calculation of activity coefficients is relatively new, and many current equilibrium studies ignore deviations in the gas phase. However, if correlating equations are deduced entirely from a study of liquid behaviour, then it appears logical that only truly liquid deviation factors should be used for correlation purposes, and not overall correction factors. Furthermore, in the Li–Coull method of correlation, the slopes of the straight line plots are considerably altered by the inclusion or omission of z-factors. Now the b_1/b_2 ratios are calculated mainly from the relation of the slopes, and inaccurate values of these ratios result if z-factors are omitted. Hence not only binary, but ternary correlation is affected. To be specific, the binary methyl*cyclo*hexane–toluene is seen in Fig 11 to be completely symmetrical, *i.e.* only one curve is required for both components. Neglect of z-factors would produce two curves of differing slopes.

PREDICTED TERNARY DATA

The graphs of predicted ternary data have demonstrated some new aspects which affect the extractive distillation process. In particular, the curves of relative volatility as a function of concentration (Fig 22) indicate that the rate of increase of α as a function of increase in furfural concentration is some direct function of the naphthene concentration, *i.e.* the rate of increase of α is greatest in the region where it is most desirable. Furthermore, α becomes independent of hydrocarbon ratios at 80 per cent furfural concentration. This confirms the work of Fenske *et al* [15] using aniline. Even more remarkable is the fact that an overall maximum of α occurs at about 90 per cent furfural. This is accounted for by the fact that above 80 per cent furfural, the bubble point temperature rapidly rises, resulting in a considerable reduction in the ratio of the activity coefficients γ_M/γ_T. This becomes so marked between 90 and 100 per cent solvent that α actually decreases. Confirmation of this is seen in Fig 28, which shows that under isothermal conditions at 130° C, the isothermal values of α still continue to rise normally as the solvent content rises from 80 to 100 per cent. (The only assumption used in the calculation of these curves is that $T \log \gamma = \text{constant}$, which is known to be reasonably true.)

Another feature of the ternary graphs is that the mutually soluble component, toluene, exhibits a decrease in activity coefficient as furfural is added to a binary hydrocarbon mixture, reaching a minimum at about 30 per cent furfural, before rising more normally. The equilibrium curve (Fig 26) becomes ever more

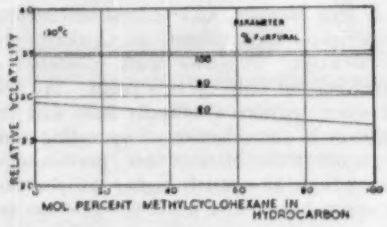

FIG 28

SYSTEM METHYL*CYCLO*HEXANE–TOLUENE–FURFURAL: RELATIVE VOLATILITY OF METHYL*CYCLO*HEXANE TO TOLUENE AT 130° C, IN HIGH CONCENTRATIONS OF FURFURAL

bowed as the solvent concentration increases. No ternary azeotrope was discovered, and it is unlikely that one exists in this system.

A NEW CRITERION OF EQUILIBRIUM

The Li–Coull equations are amongst the few practical isobaric equations yet produced for ternary systems. This raises a question as to whether isobaric or isothermal data should be sought. As most distillation operations are approximately isobaric, from the practical aspect, isobaric equilibrium data are desirable. However, nearly all the present correlating equations are based on the Gibbs–Duhem equation, which normally assumes isothermal conditions. Great need exists at the moment for isobaric equations in which γ is expressed as a function of temperature and composition. The relation $T \log \gamma = \text{constant}$ seems to hold reasonably well over the temperature ranges involved in the present work and with the types of systems encountered. It is believed that the Li–Coull equations are quite valuable as a powerful criterion of equilibrium, at least with the present type of mixtures, when developed in the following manner.

The authors point out that in any given binary the b_1/b_2 ratio can be obtained by four different methods as

$$b_1/b_2 = \left(\frac{I_2}{I_1}\right)^2 = \left(\frac{S_1}{S_2}\right)^4 = \frac{S_1}{I_1} = \frac{I_2}{S_2}. \quad (31)$$

It is concluded from this work and earlier investigations, that in reliable true equilibrium data these four values should agree very closely. This is borne out by the values obtained in this investigation.

The Li–Coull equations demand certain relationships which are not stressed in the original paper. These are best demonstrated graphically, as in Figs 29 and 30.

First, consider a "symmetrical" system. One curve of the type

$$Y = S \,.\, X + I \quad . \quad . \quad . \quad (32)$$

holds for both components, where $Y = (T \log \gamma)^{-\frac{1}{2}}$, X being the mol ratio; S and I slope and intercept respectively. In this case $b_1 = b_2$ and hence $S = I$, and equation (32) becomes

$$Y = S \,.\, X + S = S(X + 1) \quad . \quad (33)$$

Hence at $X = 0,\ Y = S = I$

$$X = 1,\ Y = 2S = 2I$$

Curve II (Fig 29) is a typical example of a symmetrical semi-ideal system, *e.g.* two hydrocarbons;

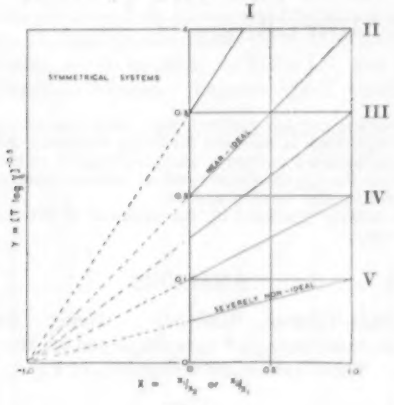

FIG 29

GENERAL LI-COULL CORRELATION CURVES FOR "SYMMETRICAL" SYSTEMS

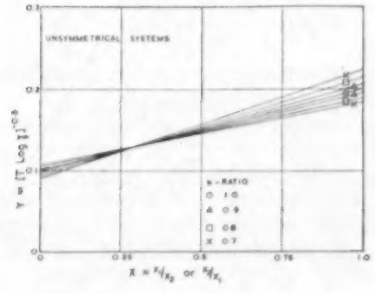

FIG 30

GENERAL LI-COULL CURVES FOR MODERATELY NON-IDEAL UNSYMMETRICAL SYSTEM; EFFECT OF VARYING b-RATIO

curve IV represents a moderately non-ideal system, *e.g.* aromatic hydrocarbon–furfural, and curve V a severely non-ideal system, which approaches immiscibility even at the boiling point, *e.g.* a paraffin–furfural mixture. Thus, depending on the slope, the intercept is fixed.

Secondly, consider the more general case of non-symmetrical systems. Each component is now represented by a straight line of the type

$$Y_1 = S_1X_1 + I_1 \quad . \quad . \quad . \quad (34)$$

$$Y_2 = S_2X_2 + I_2 \quad . \quad . \quad . \quad (35)$$

At the point of intersection,

$$Y_1 = Y_2 \text{ and } X_1 = X_2 = X^*$$

Eliminating Y_1 and Y_2

$$X_1 = X_2 = \frac{I_2 - I_1}{S_1 - S_2} \quad . \quad . \quad (36)$$

Using the relations of equation (31),

$$S_1 = I_2^2/I_1 \text{ and } S_2 = I_1^2/I_2$$

Hence the abscissa value X^*, at the intersection is given by

$$X^* = \frac{I_1I_2}{I_2^2 + I_1I_2 + I_1^2} \quad . \quad . \quad (37)$$

or

$$\frac{1}{X^*} = \frac{I_2^2 + I_1^2}{I_1I_2} + 1 \quad . \quad . \quad . \quad (38)$$

simplifying to

$$\frac{1}{X^*} = \frac{I_2}{I_1} + \frac{I_1}{I_2} + 1 = \sqrt{\frac{b_1}{b_2}} + \sqrt{\frac{b_2}{b_1}} + 1 \quad . \quad (39)$$

The ratio b_1/b_2 is thought to be the ratio of the partial molar volumes, and rarely exceeds a value of 2·0 in practice. It can be seen from Table VIII, that the position of intersection is virtually constant, regardless of the b-ratio.

TABLE VIII

Relationship Between b_1/b_2 *and* X^*

b_1/b_2	X^*	b_1/b_2	X^*
1·0	0·333	1·5	0·329
1·1	0·333	2·0	0·321
1·25	0·332	2·5	0·311

Fig 30 shows the effect of varying the b-ratio in a hypothetic system of moderate non-ideality from 1·0 to 0·7. As the b-ratio deviates from unity, the ratio of the slopes increases, but all the lines virtually pass through one common point of intersection at X^*.

The second criterion of equilibrium involves the average ordinate value Y' at the equimolar concentration $x_1/x_2 = X = 1$, and the average intercept value $I' = \dfrac{I_1 + I_2}{2}$.

Starting from equations (34) and (35), putting X_1 and X_2 equal to unity,

$$Y_1 = S_1 + I_1 \quad . \quad . \quad . \quad (40)$$

$$Y_2 = S_2 + I_2 \quad . \quad . \quad . \quad (41)$$

Eliminating S_1 and S_2 as previously indicated,

$$Y_1 = \frac{I_2^2 + I_1^2}{I_1}; \quad Y_2 = \frac{I_1^2 + I_2^2}{I_2} \quad . \quad . \quad (42)$$

$$Y' = \frac{Y_1 + Y_2}{2} = \frac{I_2 + I_1}{2}\left[\frac{I_2^2 + I_1^2}{I_1I_2}\right] \quad . \quad (43)$$

i.e. $Y' = I'(\sqrt{b_1/b_2} + \sqrt{b_2/b_1}) \quad . \quad . \quad . \quad . \quad (44)$

For a symmetrical system, (44) becomes

$$Y' = 2I' \quad . \quad . \quad . \quad . \quad (45)$$

and from the Table IX, it can be seen that the influence of the b-ratio is very small, for all practical cases.

TABLE IX

Relationship Between b_1/b_2 *and* $\sqrt{b_1/b_2} + \sqrt{b_2/b_1}$

b_1/b_2	$\sqrt{b_1/b_2} + \sqrt{b_2/b_1}$	b_1/b_2	$\sqrt{b_1/b_2} + \sqrt{b_2/b_1}$
1·0	2·0	1·5	2·041
1·1	2·002	2·0	2·121
1·25	2·012	2·5	2·213

When it is realized that the highest b-ratio in any of the systems investigated in this paper is under 1·1, it is reasonable to assert that, as the second criterion, the average $(T \log \gamma)^{-1}$ value at 50–50 concentration is twice the average value of the intercepts.

Unless association effects are present, or the constancy of the product $(T \log \gamma)_{x_1 x_2}$ is in doubt, over the temperature range of the system, data which fail to conform to these two criteria are liable to suspicion, at least with the types of systems investigated in these papers.

PART II. BINARY AND TERNARY DATA FOR THE SYSTEM *n*-HEPTANE–TOLUENE–FURFURAL

SUMMARY

Isobaric equilibrium data are presented for the system *n*-heptane–toluene–furfural, and those constituent binary systems not already included in Part I. A new binary azeotrope is reported involving *n*-heptane and furfural. Excepting the toluene–furfural binary system, which, as reported in Part I, was investigated on both the Gillespie and Fenske stills, the remaining systems were investigated using the Fenske still, at 760 mm pressure.

The Li–Coull correlation method as described in Part I was used for this ternary system.

The ease of separation of the C_7 paraffin–aromatic binary is greatly increased by the presence of furfural. Analytical data for the ternary system are presented for the first time.

INTRODUCTION

A GENERAL and theoretical introduction to vapour–liquid equilibrium, as it appertains to this present study is presented in Part I. Furthermore, the apparatus described in Part I was used without modification for the work described herein.

MATERIAL EMPLOYED

The only new material employed in this study was *n*-heptane. The commercial material, as received from Phillips Petroleum Co., had a purity of approximately 99·2 per cent; ordinary fractional distillation was not effective in eliminating the impurities, and it was necessary to employ azeotropic distillation (with methyl alcohol as entrainer) to obtain a purity corresponding to a refractive index within 0·0002 of that quoted by the API. Assuming the impurity to be *iso*-octane, the material obtained thus would be 99·9 per cent heptane. The heptane–methanol azeotrope (b.p. 59·1° C, 48·5 per cent heptane) was obtained overhead, water-washed, and finally dried over metallic sodium.

PROCEDURE

Operation of the stills and preparation of mixtures was similar to that described in Part I. For the ternary system investigation, furfural contents of approximately 20, 40, 60, and 80 mol per cent (liquid phase) were used, various hydrocarbon ratios being employed at each solvent level.

ANALYSIS

Heptane–Toluene. Refractive Index data of Bromiley and Quiggle [6] were employed for the present study. These values are also shown in Fig 3.

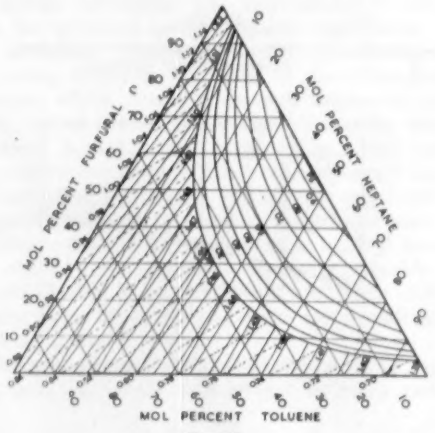

FIG 31

SYSTEM HEPTANE–TOLUENE–FURFURAL. ANALYTICAL DIAGRAM

The solid lines represent lines of constant refractive index (n_D^{20}).

The broken lines represent lines of constant density (ρ_4^{20}).

The solid curves represent curves of constant miscibility temperature (° C).

Heptane–Furfural. This binary is similar in behaviour to the methyl*cyclo*hexane–furfural system. However, the critical solution temperature was

higher, being approximately 94° C. The method of analysis employed was identical to that used for the former binary.

Heptane–Toluene–Furfural. As a result of the difficulty in water-extracting 100 per cent of the furfural from ternary mixtures, when the toluene content of the hydrocarbon pair was high, such mixtures as were single phase above about 10° C were analysed by a combined refractive index–density method. The analytical data of this system are presented in Fig 31.

Mixtures less rich in toluene were analysed by the physico-chemical method outlined in Part I.

RESULTS

Vapour pressure data for normal heptane presented in Table II, and vapour-phase correction factors (z) (at 760 mm) are to be found in Table III, and Fig 5.

(1) *Heptane–Toluene.* Vapour–liquid equilibrium

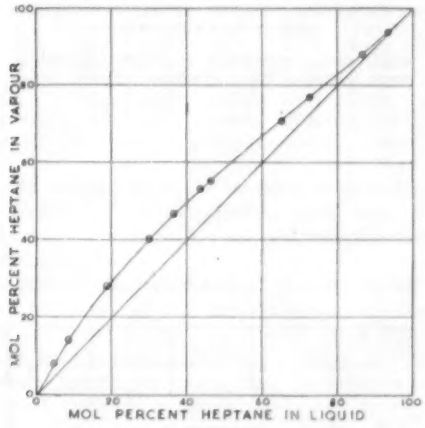

Fig 32

SYSTEM HEPTANE–TOLUENE. EQUILIBRIUM DIAGRAM

○ Experimental values

The solid curve is derived from equations (46) and (47).

data for this system were obtained using a Fenske-type still, equipped with the simple non-jacketed sampling cup. Figs 32 to 35 portray the equilibrium (x–y) curve, temperature–composition, relative volatility–composition, and activity coefficient curves for this system.

Values of $(T \log \gamma)^{0.5}$ for each component are plotted as a function of the liquid mol ratio in Fig 10. It can be seen that this paraffin–aromatic binary is slightly more non-ideal than the corresponding C_7 naphthene–aromatic system discussed in Part I. In contrast to the previous system, however, the Li–Coull correlation (Fig 10) takes the form of two straight lines, indicating an asymmetric system, the heptane curve having the greater slope. The curves were drawn by the method of least squares, with weighted values between ordinates of 0·1 and 1·00.

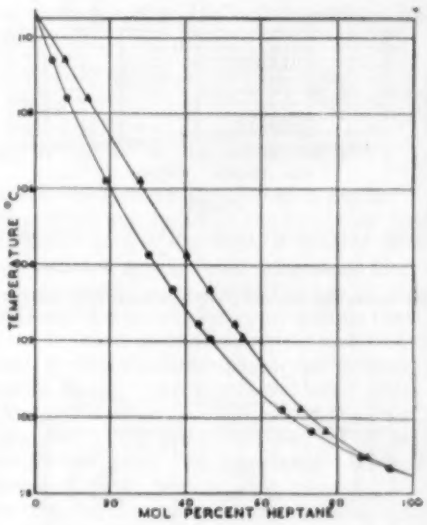

Fig 33

SYSTEM HEPTANE–TOLUENE. TEMPERATURE–COMPOSITION CURVES

○ Liquid-experimental values

△ Vapour-experimental values

The solid curves are derived from equations (46) and (47).

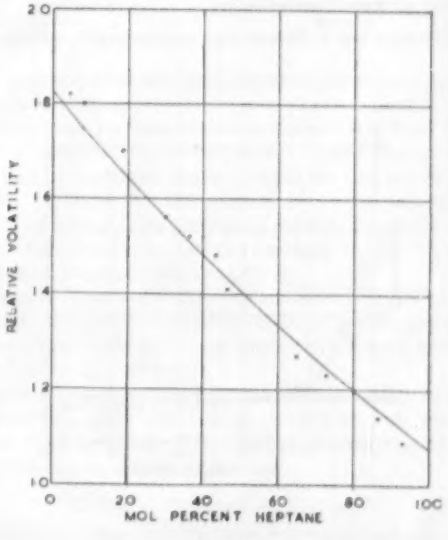

Fig 34

SYSTEM HEPTANE–TOLUENE. RELATIVE VOLATILITY OF HEPTANE TO TOLUENE

○ Experimental values

The solid line is derived from equations (46) and (47).

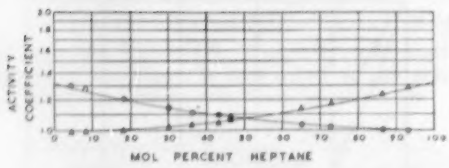

FIG 35

SYSTEM HEPTANE–TOLUENE. ACTIVITY COEFFICIENTS

○ Heptane △ Toluene

The curves are derived from equations (46) and (47).

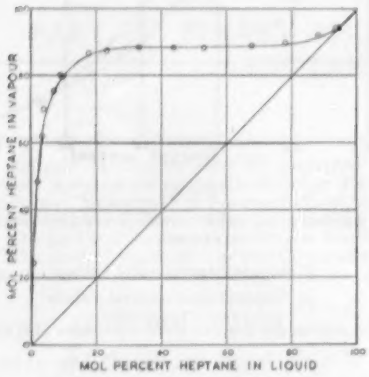

FIG 36

SYSTEM HEPTANE–FURFURAL. EQUILIBRIUM DIAGRAM

○ Experimental values △ Azeotrope

The solid line is derived from equations (49) and (50).

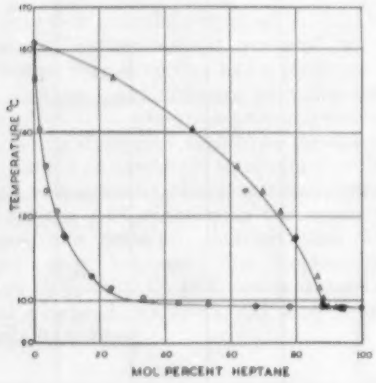

FIG 37

SYSTEM HEPTANE–FURFURAL. TEMPERATURE–COMPOSITION CURVES

○ Experimental values (liquid)

△ Experimental values (vapour)

□ Azeotrope

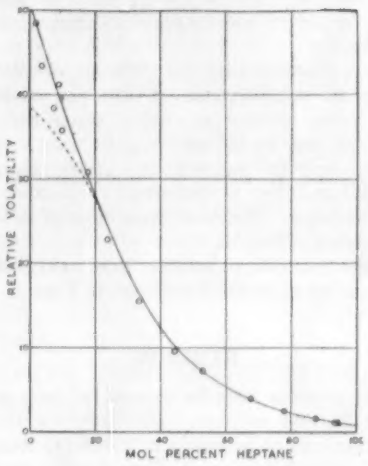

FIG 38

SYSTEM HEPTANE–FURFURAL. RELATIVE VOLATILITY OF HEPTANE TO FURFURAL

The solid curve represents experimental values. The broken curve is derived from equations (49) and (50).

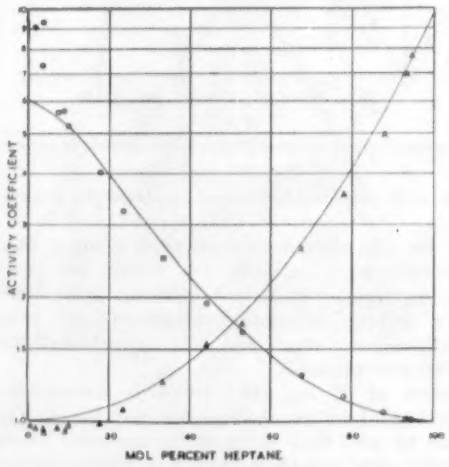

FIG 39

SYSTEM HEPTANE–FURFURAL. ACTIVITY COEFFICIENTS

○ Experimental values—heptane

△ Experimental values—furfural

The curves are derived from equations (49) and (50).

From these curves were developed the following Li–Coull type equations :

$$T \log \gamma_H = \frac{43{\cdot}9x_T^2}{(x_H + 0{\cdot}987x_T)^2} \quad . \quad (46)$$

$$T \log \gamma_T = \frac{45{\cdot}6x_H^2}{(x_T + 1{\cdot}013x_H)^2} \quad . \quad (47)$$

The calculated relative volatility is expressed as

$$\alpha_{calc} = \frac{p_H \gamma_H z_T}{p_T \gamma_T z_H} \quad . \quad . \quad . \quad (48)$$

By the method outlined in Part I, predicted values of T, γ_H and γ_T, α_{calc}, y_H and y_T can be obtained. These values are listed in Table X, and the curves drawn

TABLE X

Heptane–Toluene Predicted Data

x_H	x_T	t, °C	y_H	y_T	γ_H	γ_T	α_{calc}
0·1	0·9	108·0	0·161	0·839	1·246	1·003	1·72
0·2	0·8	105·9	0·291	0·709	1·191	1·011	1·64
0·3	0·7	104·2	0·401	0·599	1·143	1·025	1·56
0·4	0·6	102·8	0·497	0·503	1·104	1·045	1·49
0·5	0·5	101·6	0·583	0·417	1·070	1·071	1·40
0·6	0·4	100·7	0·666	0·334	1·044	1·104	1·33
0·7	0·3	99·9	0·750	0·250	1·025	1·145	1·28
0·8	0·2	99·2	0·827	0·173	1·011	1·193	1·20
0·9	0·1	98·8	0·911	0·089	1·002	1·250	1·13

in Fig 32 through 35 represent these predicted values.

(2) *Heptane–Furfural.* This system was investigated using a Fenske still, equipped with the vacuum-jacketed receiver.

The general characteristics of this binary are very similar to those of the methyl*cyclo*hexane–furfural binary discussed above. It is even more non-ideal, and the bubble-point–composition curve is virtually isothermal for 85 per cent of the composition range. Analytical methods employed were similar to those used for the above-mentioned binary. Table XI

TABLE XI

Heptane–Furfural Predicted Data

x_H	x_F	t	y_H	y_F	γ_H	γ_F	α_{calc}
0·1	0·9	114·0	0·784	0·216	5·262	1·019	34·13
0·2	0·8	102·3	0·868	0·132	3·960	1·082	27·44
0·3	0·7	98·7	0·886	0·114	2·939	1·201	18·83
0·4	0·6	98·3	0·891	0·109	2·236	1·393	12·39
0·5	0·5	98·7	0·888	0·112	1·762	1·690	7·97
0·6	0·4	99·2	0·885	0·115	1·445	2·158	5·13
0·7	0·3	99·2	0·884	0·116	1·235	2·897	3·28
0·8	0·2	98·9	0·892	0·108	1·100	4·103	2·06
0·9	0·1	98·4	0·921	0·079	1·024	6·152	1·28

and Figs 36 to 39 correspond exactly to those developed for other binary systems described in this paper. The same conclusions, as already drawn from the naphthene–furfural study, regarding the probability of flashing of vapours from the condensate receiving cup, apply for the range 0–10 per cent heptane in the liquid phase.

The corresponding Li–Coull equations for this system are :

$$T \log \gamma_H = \frac{396{\cdot}5x_F^2}{(x_H + 1{\cdot}080x_F)^2} \quad . \quad (49)$$

$$T \log \gamma_F = \frac{315{\cdot}3x_H^2}{(x_F + 0{\cdot}926x_H)^2} \quad . \quad (50)$$

and the Li–Coull curves are plotted in Fig 20.

Few systems can approach the two-phase condition more closely at the atmospheric boiling point, the critical solution temperature being only 5° C lower. This characteristic necessitated the use of preheated cooling water for the condenser with those runs which involved between approximately 40 and 60 per cent heptane in the distillate phase, to prevent phase separation in the vacuum-jacketed cup. Also, great care had to be taken in withdrawing the condensate samples, and every precaution had to be taken to exclude water from the apparatus. As with the naphthene–furfural system, the severely non-ideal nature of the system prevents the Li–Coull equations from applying exactly, particularly in the calculation of temperature–composition curves. The error is not great, however, but the curve as drawn in Fig 37 is based on experimental evidence.

The relative volatility curve indicates the presence of an azeotrope at approximately 95 mol per cent heptane. This azeotrope was confirmed by fractionation of a 95/5 mixture in a thirty-plate column at a reflux ratio of 25 : 1. The azeotrope has the following properties :

Composition . . .	94·5 mol per cent heptane 5·5 mol per cent furfural
Boiling point . . .	98·3° C/760 mm
Miscibility point . .	18° C

This azeotrope has not been reported previously in the literature.

The *toluene–furfural* system is described in Part I.

(3) *Heptane–Toluene–Furfural.* This ternary system was investigated under conditions and procedure similar to those for the system methyl*cyclo*hexane–toluene–furfural. As previously stated, the method of analysis adopted was varied according to the toluene content of the hydrocarbon pair.

Correlated data for this system were calculated by precisely the same method as outlined previously and are listed in Table XII, and the system is graphically described by Figs 40 to 45.

Again it is evident that the relative volatility of the hydrocarbon pair reaches a maximum at about 90 per cent furfural. The correlations are based on the following equations :

$$T \log \gamma_H = \frac{43{\cdot}9x_T^2 + 396{\cdot}5x_F^2 + 263{\cdot}4x_T x_F}{(x_H + 0{\cdot}987x_T + 1{\cdot}080x_F)^2} \quad . \quad (51)$$

$$T \log \gamma_T = \frac{45{\cdot}6x_H^2 + 162{\cdot}8x_F^2 - 171{\cdot}9x_H x_F}{(x_T + 1{\cdot}013x_H + 1{\cdot}094x_F)^2} \quad . \quad (52)$$

$$T \log \gamma_F = \frac{315{\cdot}3x_H^2 + 123{\cdot}8x_T^2 + 395{\cdot}5x_H x_T}{(x_F + 0{\cdot}926x_H + 0{\cdot}914x_T)^2} \quad (53)$$

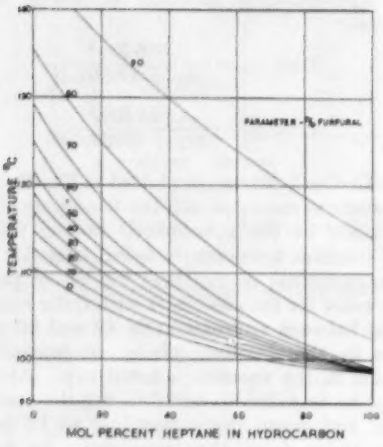

FIG 40

SYSTEM HEPTANE–TOLUENE–FURFURAL. TEMPERATURE–COMPOSITION CURVES

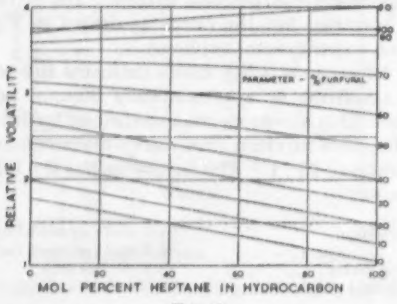

FIG 41

SYSTEM HEPTANE–TOLUENE–FURFURAL. RELATIVE VOLATILITY OF HEPTANE TO TOLUENE IN THE PRESENCE OF FURFURAL

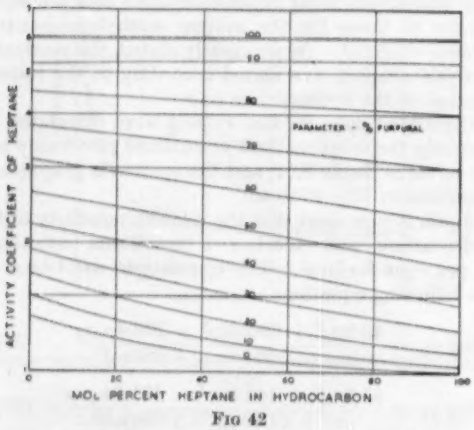

FIG 42

SYSTEM HEPTANE–TOLUENE–FURFURAL: ACTIVITY COEFFICIENT OF HEPTANE

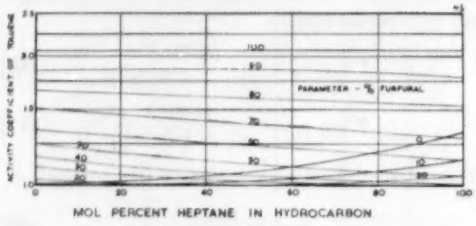

FIG 43

SYSTEM HEPTANE–TOLUENE–FURFURAL: ACTIVITY COEFFICIENT OF TOLUENE

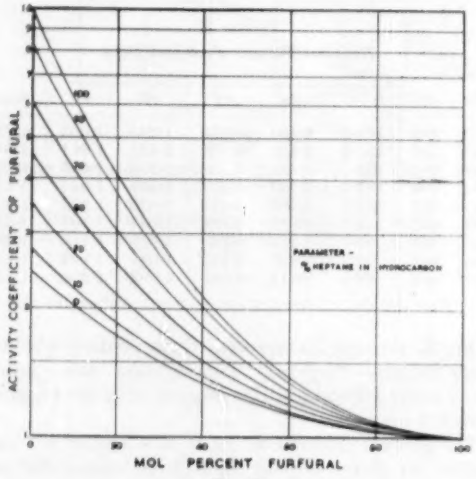

FIG 44

SYSTEM HEPTANE–TOLUENE–FURFURAL: ACTIVITY COEFFICIENT OF FURFURAL

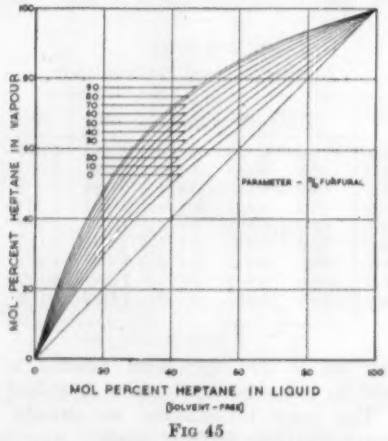

FIG 45

SYSTEM HEPTANE–TOLUENE–FURFURAL: EFFECT OF FURFURAL ON THE VAPOUR–LIQUID EQUILIBRIUM CURVE OF THE HYDROCARBON BINARY

TABLE XII

Heptane–Toluene–Furfural Predicted Data

Liquid composition			Predicted data								
x_F	x_H	x_T	t, °C	y_H *	γ_H	γ_T	γ_F	α_{HT}	y_H	y_T	y_F
0·10	0·09	0·81	109·5	0·176	1·388	1·003	2·214	1·920	0·168	0·789	0·043
	0·27	0·63	105·3	0·429	1·260	1·002	2·691	1·760	0·410	0·545	0·045
	0·45	0·45	102·5	0·616	1·163	1·019	3·329	1·600	0·585	0·365	0·050
	0·63	0·27	100·5	0·774	1·091	1·054	4·195	1·445	0·727	0·214	0·059
	0·81	0·09	99·0	0·922	1·042	1·110	5·395	1·325	0·857	0·072	0·071
0·20	0·08	0·72	111·2	0·190	1·573	1·023	1·848	2·125	0·176	0·748	0·076
	0·24	0·56	106·5	0·458	1·423	1·005	2·153	1·975	0·424	0·502	0·074
	0·40	0·40	103·3	0·646	1·302	1·000	2·542	1·825	0·595	0·326	0·079
	0·56	0·24	101·2	0·798	1·204	1·009	3·047	1·680	0·727	0·186	0·087
	0·72	0·08	99·5	0·934	1·131	1·031	3·706	1·550	0·840	0·060	0·100
0·30	0·07	0·63	112·8	0·206	1·811	1·066	1·581	2·345	0·185	0·711	0·104
	0·21	0·49	107·5	0·485	1·643	1·035	1·775	2·205	0·439	0·465	0·096
	0·35	0·35	104·0	0·673	1·497	1·014	2·012	2·065	0·609	0·295	0·096
	0·49	0·21	101·5	0·819	1·376	1·002	2·308	1·930	0·735	0·163	0·102
	0·63	0·07	99·9	0·941	1·276	1·002	2·673	1·795	0·838	0·052	0·110
0·40	0·06	0·54	114·5	0·224	2·121	1·129	1·391	2·585	0·195	0·676	0·129
	0·18	0·42	108·5	0·515	1·936	1·087	1·512	2·475	0·456	0·431	0·113
	0·30	0·30	105·0	0·698	1·770	1·055	1·657	2·32	0·621	0·270	0·109
	0·42	0·18	102·1	0·839	1·625	1·029	1·829	2·22	0·746	0·146	0·108
	0·54	0·06	100·2	0·950	1·499	1·013	2·036	2·085	0·842	0·045	0·113
0·50	0·05	0·45	116·6	0·240	2·521	1·216	1·251	2·84	0·203	0·641	0·156
	0·15	0·35	109·8	0·541	2·324	1·169	1·325	2·755	0·471	0·399	0·130
	0·25	0·25	105·1	0·726	2·148	1·130	1·409	2·66	0·641	0·242	0·117
	0·35	0·15	101·8	0·855	1·977	1·093	1·510	2·54	0·761	0·128	0·111
	0·45	0·05	99·6	0·957	1·829	1·064	1·626	2·425	0·850	0·039	0·111
0·60	0·04	0·36	119·4	0·257	3·028	1·332	1·150	3·100	0·209	0·604	0·187
	0·12	0·28	111·5	0·568	2·847	1·285	1·193	3·060	0·484	0·368	0·148
	0·20	0·20	105·8	0·748	2·660	1·241	1·242	2·990	0·650	0·217	0·133
	0·28	0·12	102·3	0·869	2·479	1·199	1·297	2·905	0·772	0·106	0·122
	0·36	0·04	99·4	0·963	2·312	1·161	1·359	2·810	0·856	0·034	0·110
0·70	0·03	0·27	123·3	0·271	3·656	1·478	1·079	3·355	0·207	0·557	0·236
	0·09	0·21	114·6	0·590	3·506	1·437	1·103	3·350	0·484	0·335	0·181
	0·15	0·15	108·3	0·769	3·358	1·395	1·127	3·345	0·659	0·196	0·145
	0·21	0·09	103·6	0·885	3·193	1·354	1·154	3·31	0·774	0·100	0·126
	0·27	0·03	100·2	0·966	3·019	1·313	1·185	3·24	0·856	0·029	0·115
0·80	0·02	0·18	129·8	0·287	4·420	1·653	1·033	3·590	0·196	0·487	0·317
	0·06	0·14	120·6	0·609	4·361	1·627	1·042	3·645	0·466	0·297	0·237
	0·10	0·10	113·5	0·787	4·270	1·598	1·053	3·685	0·641	0·173	0·186
	0·14	0·06	108·1	0·897	4·156	1·565	1·064	3·69	0·756	0·088	0·156
	0·18	0·02	103·8	0·970	4·028	1·531	1·075	3·685	0·839	0·025	0·136
0·90	0·01	0·09	141·0	0·294	5·270	1·856	1·008	3·75	0·147	0·351	0·502
	0·03	0·07	133·1	0·620	5·313	1·851	1·009	3·835	0·377	0·230	0·393
	0·05	0·05	126·6	0·795	5·322	1·841	1·012	3·895	0·544	0·139	0·317
	0·07	0·03	120·9	0·901	5·318	1·828	1·014	3·96	0·664	0·072	0·264
	0·09	0·01	116·3	0·972	5·284	1·810	1·018	4·00	0·759	0·021	0·220
1·0	0·00	0·00	161·7	0·000	6·054	2·055	1·000	3·745	0·000	0·000	1·000

* Expressed on solvent free basis.

DISCUSSION

As before, the ternary system is completely described algebraically by using constants derived only from the constituent binary systems. Ternary constants are avoided by the introduction of a temperature factor into all the correlating equations, in the form of $T \log \gamma$.

Study of the paraffin–furfural binary tends to confirm the conclusions already reached in previous studies, that the Fenske still is not suitable for mixtures which exhibit a large temperature difference between liquid and "vapour condensate" boiling points.

PART III. BINARY AND TERNARY DATA FOR THE SYSTEM METHYL*CYCLO*HEXANE–*n*-HEPTANE–FURFURAL

SUMMARY

Isobaric equilibrium data at 760 mm pressure are presented for the ternary system methyl*cyclo*hexane–*n*-heptane–furfural, and for the one constituent binary system which has not been presented in early parts of this paper. All experimental work was conducted in the Fenske-type still previously described, and the Li–Coull equations were employed for correlation of the experimental results. The ease of separation of the paraffin–naphthene binary is greatly increased by the presence of furfural in the liquid phase, although the improvement obtainable is by no means as effective as in the other cases studied. This is due to the fact that the hydrocarbon pair exhibits nearly ideal solution conditions when no solvent is present, and each hydrocarbon develops a very similar degree of non-ideality at any particular furfural concentration.

INTRODUCTION

THE experimental and theoretical principles of Part III are based entirely on those already outlined in Parts I and II. Furfural concentrations of approximately 20, 40, 60, and 80 mol per cent (liquid phase) were used for the ternary study, and four runs were made at each solvent level, with varying hydrocarbon ratios.

ANALYSIS

Methyl*cyclo*hexane–*n-Heptane* mixtures were analysed by refractive index. Data from two sources [6, 16] were used, and are shown in Fig 3.

*Methyl*cyclo*hexane–n-Heptane–Furfural.* Unlike the previous two ternary systems, this system contained no toluene, and all mixtures encountered were two-phase at 20° C. Hence no difficulties were involved in obtaining complete extraction of furfural, which was estimated by the chemical methods previously outlined.

EXPERIMENTAL RESULTS

(1) *Methyl*cyclo*hexane–n-Heptane.* All determinations were made in a Fenske-type still, employing a simple condensate cup.

TABLE XIII

*n-Heptane–Methyl*cyclo*hexane Equilibrium Data: Activity Coefficients*

Run no.	Mol % x_M	Mol % x_H	Mol % y_M	Mol % y_H	Temp, °C	α_{HM}	γ_H	γ_M
MH 26	6·75	93·25	6·35	93·65	98·2	1·068	1·001	1·006
25	15·20	84·80	14·35	85·65	98·6	1·069	1·005	1·006
3	21·95	78·05	20·90	79·10	98·85	1·064	1·007	1·013
24	32·50	67·50	31·10	68·90	98·85	1·066	1·008	1·013
23	44·35	55·65	42·70	57·30	99·15	1·069	1·009	1·011
6	50·95	49·05	49·25	50·75	99·35	1·070	1·008	1·009
7	59·80	40·20	58·05	41·95	99·6	1·075	1·010	1·006
22	60·75	39·25	59·15	40·85	99·6	1·068	1·007	1·009
8	69·30	30·70	67·80	32·20	99·9	1·072	1·007	1·007
9	78·50	21·50	77·35	22·65	100·2	1·069	1·004	1·005
10	88·20	11·80	87·45	12·55	100·5	1·074	1·004	1·004
21	94·85	5·15	94·45	5·55	100·7	1·042	1·012	1·003

Experimental values of liquid and vapour equilibrium compositions are listed in Table XIII, together with equilibrium temperatures, the experimental values of relative volatility, and experimental activity coefficients for each component γ_M and γ_H (corrected for non-ideal vapour-phase conditions as outlined above).

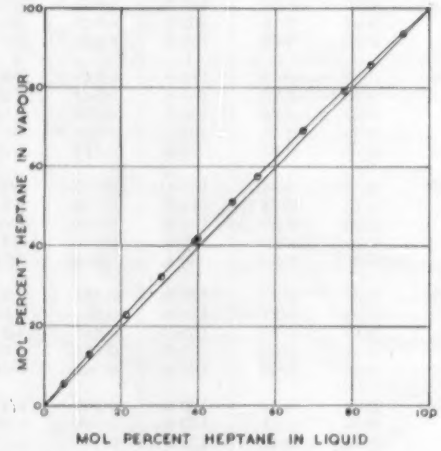

FIG 46

SYSTEM HEPTANE–METHYL*CYCLO*HEXANE: EQUILIBRIUM DIAGRAM

○ Experimental values

The solid curve is based on the assumption that the binary is an ideal system.

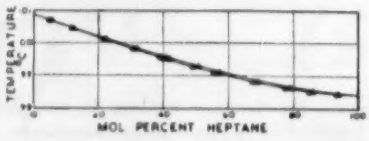

FIG 47

SYSTEM HEPTANE–METHYL*CYCLO*HEXANE: TEMPERATURE–COMPOSITION CURVE

○ Experimental values (liquid)
△ Experimental values (vapour)

The solid curves assume that the activity coefficients of both compounds are unity throughout.

Figs 46, 47, and 48 show the equilibrium, temperature–composition, and relative volatility curves for this binary. The activity coefficients are exceedingly close to unity; they are certainly too close to allow the function $(T \log \gamma)^{-0.5}$ to be used for correlation purposes.

Assuming for the moment that the system is ideal, it is possible to calculate the total pressure of the system from the other experimental data. This falls from 760 mm for the pure components to 753 mm for a 50–50 mixture, suggesting that the system is not quite ideal in its behaviour, but that the end-values of the activity coefficient curves lie in the region of 1·010. In Fig 48 the solid curve represents the relative volatility based on ideal liquid behaviour, whilst the dotted curve is based on an end-γ-value of 1·010 for each component. It may be seen that the latter curve agrees more closely with the experimental figures. Analytical difficulties arise with this system because of the small range of refractive index involved.

(2) *Methylcyclohexane–n-Heptane–Furfural.* Correlated equilibrium data are listed in Table XIV, using the constants of the two-constituent binary furfural–hydrocarbon correlations. For purposes of correlation the hydrocarbon binary has been assumed ideal, as the constants $\frac{k_{12}}{b_1}$ and $\frac{k_{12}}{b_2}$ in the ternary equations for this system are too small to warrant inclusion. The function $\frac{b_H}{b_M}$ was calculated as the mean of the functions $\frac{b_H/b_T}{b_M/b_T}$ and $\frac{b_H/b_F}{b_M/b_F}$ derived from other binary studies in this series. The full correlating equations for this system are :

$$T \log \gamma_H = \frac{1{\cdot}9x_M^2 + 396{\cdot}5x_F^2 + 34{\cdot}3x_Mx_F}{(x_H + 1{\cdot}007x_M + 1{\cdot}080x_F)^2} \quad . \quad (54)$$

$$T \log \gamma_M = \frac{1{\cdot}7x_H^2 + 349{\cdot}8x_F^2 - 45{\cdot}6x_Hx_F}{(x_M + 0{\cdot}993x_H + 1{\cdot}050x_F)^2} \quad . \quad (55)$$

$$T \log \gamma_F = \frac{315{\cdot}3x_H^2 + 303{\cdot}6x_M^2 + 612{\cdot}4x_Hx_M}{(x_F + 0{\cdot}926x_H + 0{\cdot}952x_M)^2} \quad (56)$$

The initial terms $1{\cdot}9\,x_M^2$ and $1{\cdot}7\,x_H^2$ in equations (54) and (55) respectively are so small that they can be neglected.

TABLE XIV

Heptane–Methylcyclohexane–Furfural Predicted Data

Liquid composition			t, °C	y_H *	γ_H	γ_M	γ_F	α_{HM}	y_H	y_M	y_F
x_F	x_H	x_M									
0·2	0·16	0·64	101·4	0·219	1·128	1·078	3·701	1·120	0·196	0·698	0·106
	0·32	0·48	100·8	0·429	1·121	1·069	3·779	1·124	0·383	0·511	0·106
	0·48	0·32	100·2	0·629	1·114	1·060	3·874	1·127	0·561	0·332	0·107
	0·64	0·16	99·6	0·820	1·107	1·052	3·979	1·127	0·731	0·162	0·107
0·4	0·12	0·48	102·1	0·225	1·492	1·374	2·052	1·163	0·198	0·681	0·121
	0·24	0·36	101·4	0·438	1·481	1·358	2·074	1·168	0·386	0·495	0·119
	0·36	0·24	100·6	0·638	1·469	1·342	2·099	1·172	0·562	0·320	0·118
	0·48	0·12	99·9	0·824	1·456	1·326	2·127	1·178	0·729	0·155	0·116
0·6	0·08	0·32	102·1	0·232	2·294	2·046	1·366	1·203	0·203	0·675	0·122
	0·16	0·24	101·2	0·446	2·278	2·024	1·371	1·207	0·393	0·488	0·119
	0·24	0·16	100·2	0·645	2·265	2·004	1·377	1·211	0·570	0·314	0·116
	0·32	0·08	99·3	0·830	2·250	1·984	1·383	1·215	0·737	0·151	0·112
0·8	0·04	0·16	106·9	0·235	3·962	3·472	1·078	1·226	0·199	0·648	0·153
	0·08	0·12	105·7	0·450	3·960	3·460	1·079	1·230	0·385	0·469	0·146
	0·12	0·08	104·4	0·650	3·962	3·449	1·080	1·234	0·558	0·302	0·140
	0·16	0·04	103·4	0·832	3·958	3·457	1·081	1·238	0·721	0·146	0·133
1·0	0·00	0·00	161·7	0·000	6·054	5·359	1·000	1·236	0·000	0·000	1·000

y_H* = mol per cent heptane, expressed on solvent-free basis.

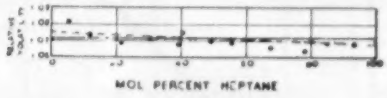

FIG 48

SYSTEM HEPTANE–METHYLCYCLOHEXANE : RELATIVE VOLATILITY OF HEPTANE TO METHYLCYCLOHEXANE

○ Experimental values

The solid line is calculated on the assumption that ideal conditions apply. The broken line is calculated on the assumption that the end values of the activity coefficient curves are 1·010 for each component.

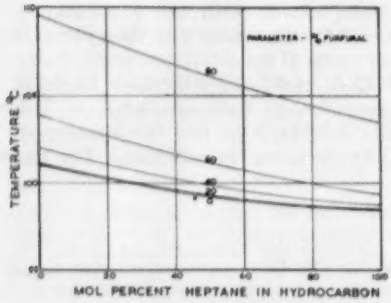

FIG 49

SYSTEM HEPTANE–METHYL*CYCLO*HEXANE–FURFURAL: TEMPERATURE–COMPOSITION CURVES

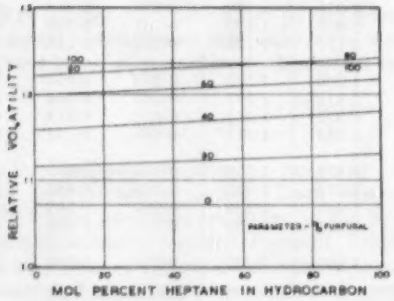

FIG 50

SYSTEM HEPTANE–METHYL*CYCLO*HEXANE–FURFURAL: RELATIVE VOLATILITY OF HEPTANE TO METHYL*CYCLO*HEXANE IN THE PRESENCE OF FURFURAL

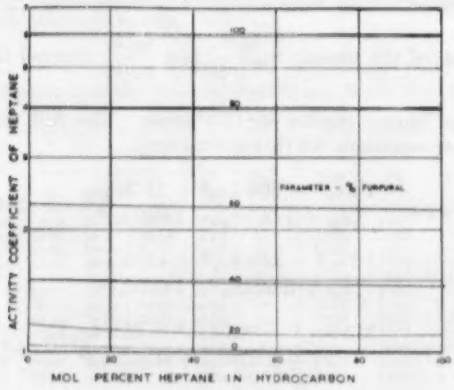

FIG 51

SYSTEM HEPTANE–METHYL*CYCLO*HEXANE–FURFURAL: ACTIVITY COEFFICIENT OF HEPTANE

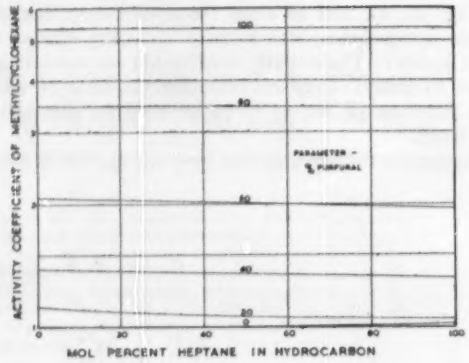

FIG 52

SYSTEM HEPTANE–METHYL*CYCLO*HEXANE–FURFURAL: ACTIVITY COEFFICIENT OF METHYL*CYCLO*HEXANE–FURFURAL

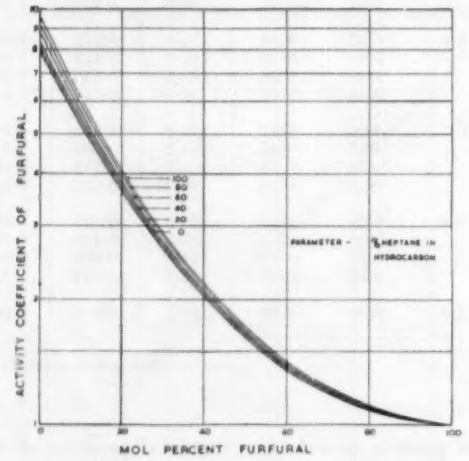

FIG 53

SYSTEM HEPTANE–METHYL*CYCLO*HEXANE–FURFURAL: ACTIVITY COEFFICIENT OF FURFURAL

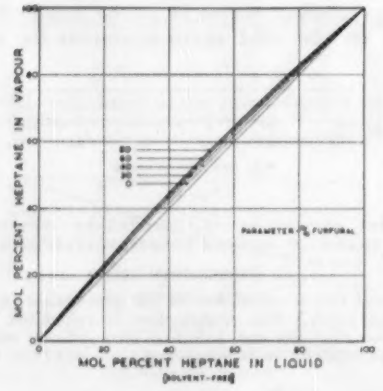

FIG 54

SYSTEM HEPTANE–METHYL*CYCLO*HEXANE–FURFURAL: EFFECT OF FURFURAL ON THE VAPOUR–LIQUID EQUILIBRIUM CURVE OF THE HYDROCARBON BINARY

DISCUSSION

The correlating equations above have been used for the preparation of Table XIV, from which Figs 49 to 54 were prepared. These describe the behaviour of this system, on a basis similar to that used for the ternary systems of Parts I and II.

As in the previous systems, the improvement in relative volatility of the key components increases up to a maximum at about 80 mol per cent furfural. In this system the improvement is from 1·07 to 1·22, as compared with maximum relative volatilities of approximately 3 obtained in the other systems.

PART IV. GENERAL CONCLUSIONS

The authors have gained considerable confidence in the Li–Coull method of correlation from the fact that three ternary systems have been correlated from data based entirely on the six constituent binary systems, each ternary system possessing two constituent binary systems which appear in one of the other ternary systems. As the same constants are common to more than one ternary system, and good agreement exists between experimental and predicted results in all three systems, it is considered that this unusually severe test imposed on the Li–Coull correlation method proves it to be a sound practical means of correlation.

LIMITATIONS OF THE LI–COULL METHOD

As increasing departure from ideality was encountered, the Li–Coull equations began to demonstrate a limitation of accuracy. Whereas most of the binary systems encountered showed a very close agreement between experimental and calculated bubble-point composition curves, the calculated bubble-point curve for the least ideal system, heptane–furfural, showed somewhat poorer agreement. It is probable that these equations are too simple to account for all phenomena—it is likely that some molecular aggregation occurs in this system, as it is known that two phases would appear at a temperature 5° C lower than the boiling point of a 50–50 mixture of heptane and furfural.

Furthermore, the constancy of the (T log γ) function may not extend for the full temperature range of 60° C exhibited by this binary.

TREATMENT OF EXPERIMENTAL RESULTS

Ternary analysis is often a difficult and lengthy process, and any correlation method, which avoids the necessity of determining specific ternary constants whilst retaining sufficient accuracy, is of great practical value. It should be emphasized, however, that, in order to obtain good correlations by this method, it is essential, particularly with the hydrocarbon systems, to correct the activity coefficient values for non-ideal vapour phase behaviour, as the slopes of the Li–Coull curves are particularly susceptible to the effect of the z-correction factors. In the case of the furfural–hydrocarbon systems, where the ratio γ/z is much greater, the importance of correcting the co-efficients is considerably less.

General Observations. In all the systems investigated it can be seen that the improvement in the relative volatility of the key components is always effected by the addition of solvent, particularly in those regions where an improvement is to be most desired.

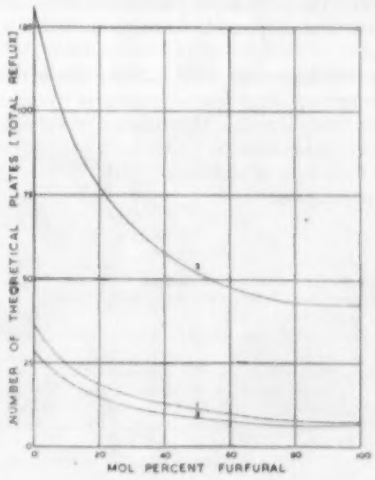

Fig 55

NUMBER OF EXTRACTIVE DISTILLATION ZONE THEORETICAL PLATES REQUIRED FOR THE CONTINUOUS SEPARATION OF 99 PER CENT PURITY PRODUCTS (AT TOTAL REFLUX), AS A FUNCTION OF FURFURAL CONCENTRATION

Curve 1—Methyl*cyclo*hexane–toluene
Curve 2—Heptane–toluene
Curve 3—Heptane–methyl*cyclo*hexane

As this project is connected with the practical separation of these hydrocarbons from a narrow boiling naphtha cut, the number of theoretical plates (at total reflux) required to separate each hydrocarbon binary pair to 99 per cent purity has been calculated using the Fenske–Underwood equation.[14, 38] The results are plotted in Fig 55, and show that although the theoretical maximum reduction in plate requirement is obtained at 80 to 90 per cent furfural, an optimum furfural concentration would exist at about 60 to 70 per cent, in that a considerable

reduction in column diameter would be effected for the same hydrocarbon throughput. In each case the reduction in tower height is approximately 70 per cent of that required with no solvent present, assuming that plate efficiency remains constant.

It is further concluded that the separation of aromatic hydrocarbons from a hydrocarbon mixture is much easier than the separation of other hydrocarbon series. This has recently been confirmed by Berti and Leidi,[4] who extractively distilled a narrow naphtha cut, obtaining pure toluene and methyl*cyclo*hexane.

This research project has been developed simultaneously with other extractive distillation projects at Birmingham University, including investigations into the operation of a 2-inch diameter 22-ft extractive distillation tower, containing approximately twenty-five to thirty theoretical plates, equipped with vapour and liquid sampling points spaced at intervals of 2 ft. It is planned to investigate initially the separation of C_7 hydrocarbon pairs on this column using furfural as solvent, and the project may at a later date incorporate the separation of pure hydrocarbons from a narrow boiling cut.

Other developments may include the investigation of the corresponding four-component system of furfural and the three hydrocarbons involved in this study, the extension to C_7-olefin hydrocarbons, and possibly the effect of addition of water to furfural on its solvent properties.

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AN APPRAISAL OF THE HIGH PRESSURE OXIDATION METHOD FOR TESTING TRANSFORMER OIL *

By J. M. WARD (Associate Fellow) †

SUMMARY

Tests on a variety of transformer oils by a slightly modified form of the high pressure oxidation method (ASTM D670-42T, Method B) are described. The oils tested include new and reconditioned oils, Continental oils, inhibited oils, and a series of experimental oils specially prepared for investigating accelerated oxidation tests. The standard deviation of results obtained with a conventional transformer oil is given. It is found that the method is simple in manipulation, requires very little attention during the oxidation period, and is particularly suitable for intermittent testing. Under standard conditions, the test does not distinguish between straight and inhibited oils but can be made to do so by using soluble catalysts, either copper or iron. The small quantities of sludge and acid produced by the standard procedure from conventional oils may be increased by using either solid or soluble catalysts.

INTRODUCTION

THE high pressure oxidation method, or bomb method, for testing the oxidation stability of transformer oil is comparatively new. It was developed by Clark [1] in the U.S.A. and issued as a " Tentative Method of Test for Sludge Formation in Mineral Transformer Oil " (designation D670–42T, Method B) by the ASTM in 1942. It is believed not to have been used before in the U.K.

An investigation of the method was undertaken, first, because good reports of it had been received from the U.S.A., secondly, because it appeared to be especially suitable for the investigations and intermittent testing required in the Research Laboratories of the British Electricity Authority, and thirdly, because E.R.A. Sub-Committee E/A (Insulating Oils—Chemical and Physical Tests), was interested, in connexion with an international investigation organized by the International Electrotechnical Commission (I.E.C.).

This paper describes tests which have been made, using the bomb, which allow of a tentative appraisal of the method. The repeatability of results obtained with an oil complying with BS 148 : 1951, using each of two bombs, has been determined. A series of British oils complying with BS 148 : 1951, including a number of reconditioned oils, has been tested, as well as a selection of Continental oils. A series of experimental oils prepared by the Thornton Research Centre of the Shell Petroleum Co. for investigating accelerated oxidation tests has been studied. A few experiments have been made with solid and soluble catalysts, and the effect of increasing the length of the test has been briefly investigated.

DESCRIPTION OF BOMB AND ANCILLARY APPARATUS

Two pressure bombs, one of which is shown in Fig 1, were made by different manufacturers in accordance with the ASTM specification,[2] which defines the dimensions of the bomb and requires it to be made of stainless steel and capable of withstanding, with safety, an internal pressure of 10,000 p.s.i. This high factor of safety is presumably intended to accommodate oils which may oxidize very rapidly under the conditions of the test. The approximate external

FIG 1

HIGH PRESSURE OXIDATION BOMB AND OIL CONTAINER

dimensions of the bomb with cap in position are : diameter 4 inches, height 9½ inches.

The body of one bomb was made from a stabilized austenitic steel (C 0·1 per cent, Mn 0·8 per cent, Cr 18 per cent, Ni 8·5 per cent, Ti 0·6 per cent) and the cover from a ferritic steel (C 0·16 per cent, Mn 0·5 per cent, Cr 16·5 per cent, Ni 2·5 per cent). The body of the second bomb was made from an austenitic steel

* MS received 26 June 1954.

† British Electricity Authority Research Laboratories.

of the same composition as the first but not stabilized with titanium, and the cover from a ferritic steel (C 0·06 per cent, Mn 0·8 per cent, Cr 17 per cent).

The oil container was made from heat-resisting glass tubing to conform to the dimensions specified by the ASTM (6 inches long, 1¼ inches internal diameter, capacity 100 ml). The rack for holding the container upright in the bomb was made from aluminium wire. The container and holder are shown in Fig 1. The aluminium shield, for wrapping around the oil container during the oxidation period to ensure cleanliness, was not considered necessary, since all lines, valves, etc., were kept perfectly clean.

The thermostatted oil bath required to heat the bomb during the oxidation period is shown in Fig 2.

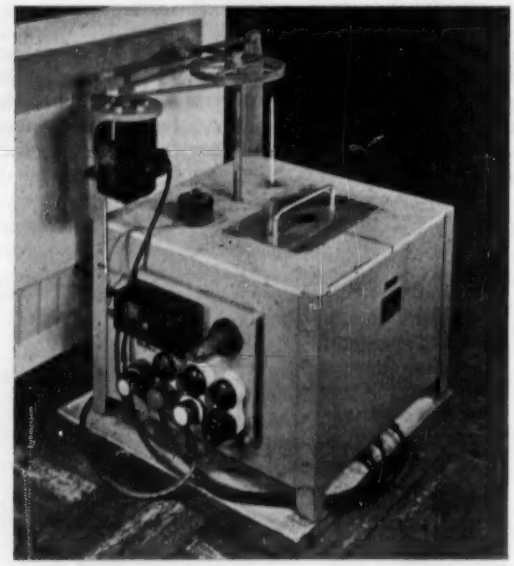

FIG 2
OIL BATH

It was electrically heated, had a cylindrical oil container, diameter 16½ inches, depth 10½ inches, and was agitated by a paddle offset from the centre to allow room for the bomb. The temperature required for the test, 140° ± 0·5° C, was adequately maintained, and the temperature across the bath was constant to within 0·1° C. The electrical loading was sufficient to return the bath to the test temperature within 20 minutes of immersing the cold bomb. By switching in an auxiliary heater, it could be returned to test temperature within 10 minutes.

DESCRIPTION OF METHOD

Briefly, 50 ml of oil are weighed into the glass container. This is placed in the clean bomb, which is filled with pure oxygen to 180 p.s.i. at 25° C. The bomb is immersed in the oil bath and heated to 140° C for 24 hours; at 140° C the pressure inside the bomb rises to 250 p.s.i. The oil container is then removed from the bomb, the sludge precipitated by adding *n*-heptane, filtered on to a sintered glass crucible, and weighed. The sludge is expressed as a percentage of the weight of the oil. The acidity of the filtrate was always determined in the work described here, although it is not called for in the ASTM standard method. The ASTM method was not followed exactly, and the departures from it and the reasons for making them are given below in the detailed description of the method.

Preparation of Sample

Wherever possible, the sample was prepared in accordance with the ASTM specification, which requires the oil to be filtered by gravity using a dried, acid-free filter paper to remove sediment, fibres, and excess water.

The oil container was cleaned with sulphuric–chromic acid cleaning mixture, washed copiously with hot water, rinsed with distilled water, and dried in an air oven at 105° to 110° C for an hour or more. It was cooled and stored in a desiccator until required. Before filling with oil it was weighed to the nearest milligram. 50 ml of the oil, filtered when necessary, were transferred to the container using a pipette fitted with a silica gel tube to prevent moisture from the breath contaminating the sample. The tube and oil were then weighed to the nearest milligram. The specification requires the weighing to be made to the nearest 0·1 mg, but this seems unnecessary, since the weight of sludge obtained is such that the determination is likely to be made with a maximum accuracy of 1 part per 1000.

Preparation of Bomb and Oxidation Procedure

The ASTM procedure of rinsing the bomb with petroleum naphtha, and after draining in air, drying in an air oven at 105° to 110° C for 3 hours was not followed. It was considered adequate, and desirable for time-saving, to rinse the bomb, including the valve, twice with acetone and twice with *n*-heptane and then to dry by passing warm, dry, filtered air into it for 20 minutes.

The container and rack were then placed in the bomb and the antimonial lead washer and steel thrust plate shown in the foreground of Fig 1 placed in position and the top screwed down and finally tightened by the six " Allen " screws.

The bomb was then twice flushed with oxygen by filling it to 5 atm (gauge) and releasing the pressure. It was then slowly filled to give the equivalent of 12¼ atm (gauge) (180 p.s.i.) at 25° C. Since Clark [1] showed that small differences in pressure had no appreciable effect on the extent of oxidation, the laboratory temperature was assumed to be at 20° C constantly and the equivalent pressure to be 12 atm (gauge).

The bomb was then placed in the oil bath and heated

for 24 hours. It was then removed, and the volume of oxygen measured immediately, at room temperature and pressure, by displacing water in an inverted 10-litre bottle. This was done to check on possible leakage during the oxidation period. After measuring the oxygen volume, the valve was closed and the bomb placed in cold water to cool it before opening. The oil container was then removed and set aside in the dark for the sludge and acidity measurement.

Measurement of Sludge and Acidity

The sludge precipitation and measurement procedure was different from that prescribed by the ASTM. Since in other tests for the I.E.C. a standard procedure had been agreed to, based on the results of an investigation into methods of precipitation of sludge after oxidation, it was decided to use this procedure in all experiments with the bomb. The oil after oxidation was allowed to stand in the dark for a period varying between one and 24 hours before diluting with ten times its volume of *n*-heptane. Initially, the period of standing before dilution was to be 24 hours, but it was found that variation between one and 24 hours was without effect on the results. After dilution the heptane–oil mixture was maintained at 25° C for one hour in a thermostatically controlled water bath. The sludge was filtered, using a No. 4 sintered glass crucible previously cleaned with hot chloroform, followed by *n*-heptane, and dried at 105° to 110° C for one hour. It was washed with a total of 150 ml of *n*-heptane, placed in an air oven for one hour at 105° to 110° C, cooled in a desiccator, and weighed. The filtered heptane–oil mixture was washed into a litre measure and the volume noted. Aliquots were then used for determining acidity.

Initially, several methods of acidity determination were investigated :

(1) *Direct Method.* 50 ml industrial methylated spirits (74 o.p.) were added to 100 ml of the heptane–oil mixture and titrated against 0·1N aqueous KOH using alkali blue as indicator.

(2) *Direct Distillation Method.* 100 ml of mixture were reduced to 50 ml by distillation of heptane, 25 ml industrial methylated spirits (74 o.p.) added and titrated as in (1).

(3) *Vacuum Distillation Method.* 100 or 200 ml of mixture distilled under vacuum (2 cm mercury) to remove all heptane. The acidity was then determined according to BS 148, Appendix H, Method A.

No appreciable difference was found between results obtained by the three methods within the range of acidities given by the conventional oils. The distillation methods gave low results with the more unstable of the experimental oils due to carry-over or distillation of acids. For the major part of the work the acidity was titrated directly. If it were required to increase the accuracy of the acidity determination the distillation method would be useful, since a larger initial sample can be taken.

ESTIMATION OF REPEATABILITY OF RESULTS

The standard deviation of results obtained by one operator using one apparatus will not necessarily give a figure for repeatability which would apply to any operator and any apparatus.[3] It serves, however, as a useful indication of repeatability, and accordingly ten determinations on an oil complying with BS 148 : 1951 were made by one operator using each of the two bombs.

Initially, discrepancies between results by the two bombs were found. The standard deviations obtained for sludge were 0·005 and 0·007 per cent; the mean values for sludge were 0·049 and 0·056 per cent. The corresponding values for acidity were 0·02 and 0·04 mg KOH/g; mean values 0·27 and 0·36 mg KOH/g.

The experiment was therefore repeated, interchanging the positions of the bombs in the bath for each pair of determinations in case there was a small difference in average temperature between the two positions : in the previous experiment the bombs were always put in the same places. In addition, only one sintered glass crucible for sludge filtration was used in conjunction with each bomb. For the previous set of determinations three had been used in conjunction with each bomb, and although these had been carefully chosen, there was a possibility that variation in porosity was affecting the sludge results. The oil used for the tests was the same as that used for the previous tests, but came from a different drum. Results are given in Table I.

TABLE I

Standard Deviation of Results on Each of Two Bombs

Bomb no.	Sludge, %				Acidity, mg KOH/g			
	Individual results		Mean	Standard deviation	Individual results		Mean	Standard deviation
	Position A	Position B			Position A	Position B		
1	0·053	0·048	0·046	0·003	0·42	0·39	0·39	0·02
	0·049	0·043			0·38	0·38		
	0·045	0·044			0·38	0·40		
	0·045	0·046			0·36	0·41		
	0·042	0·042			0·40	0·38		
2	0·049	0·047	0·047	0·003	0·43	0·41	0·41	0·03
	0·042	0·046			0·40	0·42		
	0·046	0·049			0·37	0·39		
	0·051	0·050			0·42	0·48		
	0·045	0·046			0·41	0·41		

It can be seen that there is good agreement between the two sets of figures and that the standard deviations of sludge results have been reduced. Statistical examination does not indicate that there is a difference between the two positions in the bath, however. Nevertheless, the suspicion remains that small differences in temperature were having an effect in the previous experiments.

Summarizing, it appears that a standard deviation of 0·005 per cent sludge, corresponding to a coefficient

of variation of 10 per cent, is attainable. The corresponding figure for acidity is 0·03 mg KOH/g (coefficient of variation 9 per cent). At the 5 per cent probability level these figures represent a repeatability of 0·014 per cent for sludge results and 0·08 mg KOH/g for acidity results (28 and 25 per cent expressed as percentages of the mean values). That is to say, the difference between any pair of results chosen at random will exceed these values in only 5 per cent of cases.[3]

With special care, *i.e.* using the same crucible throughout, the standard deviation of sludge results may be reduced to 0·003 per cent (coefficient of variation 7 per cent). At the 5 per cent probability level this represents a repeatability of 0·008 per cent (18 per cent expressed as a percentage of the mean value).

TESTS ON VARIOUS TYPES OF OILS BY THE STANDARD PROCEDURE

Tests on British Oils complying with BS 148 : 1951

Table II gives typical results obtained on oils complying with BS 148 : 1951. Some of these were new oils, and others were used oils which had been re-refined by oil suppliers. Results obtained in other laboratories on some of the oils by the BS 148 : 1951 oxidation test are given for comparison.

TABLE II

New and Reconditioned Oils Complying with BS 148 : 1951

Description of sample	Pressure oxidation test		BS 148 : 1951 oxidation test	
	Sludge, %	Acidity, mg KOH/g	Sludge, %	Acidity, mg KOH/g
New Oil :				
Ex Supplier A .	0·013	0·15	—	—
Ex Supplier B .	0·023	0·18	0·86	0·97
Ex Supplier C				
Sample 1 . .	0·021	0·12	0·78	1·43
Sample 2 . .	0·053	0·31	0·95	1·57
Reconditioned Oil :				
A . . .	0·060	0·30	0·91	1·28
B . . .	0·038	0·42	0·82	1·21
C . . .	0·041	0·40	0·98	2·50
D . . .	0·035	0·20	0·85	1·60

Each figure is the mean of two determinations.

It can be seen that oils complying with the British specification gave sludge results by the pressure oxidation test between about 0·015 and 0·060 per cent and acidity results between 0·12 and 0·42 mg KOH/g. In general, the new oils gave lower results than the reconditioned oils, although the results by the BS 148 test were similar.

The test appears to be more sensitive to small differences between oils than the British test. Sample 1 was from a stock of BS 148 oil set aside by Supplier C for experimental purposes. It was tested in March 1952. Sample 2 from a second drum of the same stock was tested in September 1953. The difference between the results by the pressure oxidation method, which in each case were the average of several determinations, was much greater than the difference between the results by the British test. It is assumed that the difference in both sets of results was due to slight changes in the oil during storage.

Tests on a Series of Continental Oils

A series of insulating oils representative of the oils in use in various Continental countries was tested in connexion with an investigation organized by the International Electro-Technical Commission to develop an internationally acceptable accelerated oxidation test. The results were found to lie within the ranges : sludge 0·013 to 0·048 per cent, acidity 0·07 to 0·02 mg KOH/g.

Oxidation tests by the BS 148 procedure were carried out on these oils by other participants in the programme, and results for three oils were found to lie just outside the specification limits for either sludge or acidity. The two highest results obtained by the pressure oxidation method were on two of the oils which lay outside the limits, but results of 0·021 per cent sludge and 0·12 mg KOH/g acidity were obtained on the third.

Tests on a Series of Experimental Oils

A series of experimental oils, prepared from the same feed stock, to cover a wide range of physical and chemical properties was tested. These oils were prepared by the Thornton Research Centre of the Shell Petroleum Co. for use in assessing the value of accelerated oxidation tests. A short description of the oils is as follows :

Experimental Insulating Oil No. 1. Solvent refined feed stock from which transformer oils are normally produced by further oleum and earth treatment.

Experimental Insulating Oil No. 2. An experimental oil produced by a combination of solvent extraction and acid treatment, the degree of refinement being somewhat less than in the case of E.I.O. 3 and E.I.O. 4.

Experimental Insulating Oils Nos. 3 *and* 4. Normal types of transformer oil differing in the relative amounts of solvent extraction and oleum treatment, No. 3 being more heavily solvent extracted than No. 4.

Experimental Insulating Oil No. 5. A normal type of transformer oil of higher aromatic content than Nos. 3 and 4.

Experimental Insulating Oil No. 6. A technical white oil produced by heavy oleum treatment of a solvent refined feed stock.

The results for sludge and acidity are given in Table III.

Results by the BS 148 : 1951 oxidation test are given for comparison; the aromatic contents are included as a rough guide to the degree of refining.

The wide range of degree of refinement of the E.I.O. oils was reflected in the results for both sludge and acidity. It has been seen that the values for sludge on the previous conventional samples ranged between 0·015 and 0·060 per cent, and the acidities between 0·07 and 0·42 mg KOH/g. E.I.O. samples 1 and 2 gave values within these ranges. However, the results by the BS 148 test on these oils show that they would not in fact be acceptable in the U.K. From the description of E.I.O. 1 it would be expected that this oil was "under-refined" by normally accepted British standards. E.I.O. 5 gave a sludge result lower than, and an acidity result equal to, the best of the previous samples. E.I.O. 4 gave a result several times greater, while the results for E.I.O. 3 and E.I.O. 6 were two orders of magnitude above the range found for the conventional samples.

TABLE III

Experimental Insulating Oils

Oil	Pressure oxidation test		BS 148 : 1951 oxidation test		Aromatic content,* % w
	Sludge, %	Acidity, mg KOH/g	Sludge, %	Acidity, mg KOH/g	
E.I.O. 1.	0·038	0·26	1·27	1·81	19·3
E.I.O. 2.	0·029	0·19	1·36	1·73	27·0
E.I.O. 3.	6·8	19·6	0·63	4·53	5·6
E.I.O. 4.	0·102	0·99	1·18	2·94	9·8
E.I.O. 5.	0·010	0·07	0·93	1·50	17·9
E.I.O. 6.	7·7	19·4	0·66	4·07	5·9

Each figure is the average of at least two determinations excepting E.I.O. 3 and E.I.O. 6.

* Determined according to Beaven, Foster, and Thompson.[5]

The appearance of these latter two oils after oxidation was quite different from all the previous samples examined. Whereas it is usual to find the oils slightly cloudy with suspended sludge, deepened in colour, and having the characteristic odour of a used oil, samples 3 and 6 were very dark, contained a fluid tarry sludge at the bottom, adhered as drops to the sides of the tube, and had a very pungent "acrylic" odour. The lead washer was coated with a thick layer of sludgy material, presumably a mixture of lead soaps. The lead showed clear signs of having been corroded after these were removed. The aluminium tube holder was badly pitted at the base, and similarly coated with a dark gummy material which was thought to be mainly aluminium soaps with some condensed acids which had run down the sides of the bomb. The bomb itself was stained inside but not pitted. The oxygen recovered from the bomb after oxidation measured only 3000 ml in one case and 3300 ml in the other. The volume recovered after E.I.O. 1, 2, and 5 samples had been oxidized was approximately the same as was put in originally, *i.e.* about 6500 ml. With E.I.O. 4 the recovery was a little lower, the volume being 6200 ml. The increase in weight of the oil sample due to oxygen absorption is usually only a few milligrams. E.I.O. 3 increased in weight by 1·29 g and E.I.O. 6 by 0·73 g.

Besides the above experimental oils, several samples with "over-refined" characteristics have been tested. Results enumerated above show that, given adequate refining facilities, used transformer oil can be reconditioned to comply with BS 148 : 1951. Somere conditioning processes, however, produce an unstable oil with a poor resistance to oxidation. Results by the pressure oxidation method for several such oils lay between the limits, sludge 1·8 to 2·5 per cent, acidity 6 to 10 mg KOH/g. BS 148 tests on these oils gave results of the order, sludge 0·7 per cent, acidity 4·5 mg KOH/g.

Tests on Inhibited Oils

Tests were made on two oils, complying with BS 148, inhibited with the three oxidation inhibitors in common use,

(*a*) 2,4-dimethyl-6-*tert*-butyl-phenol (24M6B),
(*b*) Phenyl-β-naphthylamine (PBN),
(*c*) 4-methyl-2,6-di-*tert*-butyl-phenol (4M26B or DBPC).

The inhibited oils were also tested by an accelerated oxygen absorption test, developed by Childs and the author, similar in principle to that described by Beaven, Irving, and Thompson.[4] In this test 5 g of oil + 100 p.p.m. oil-soluble copper as copper naphthenate are heated at 120° C in an atmosphere of oxygen. As soon as the induction period is over and the oil begins to oxidize, the change in pressure brought about by oxygen absorption breaks a circuit controlling a clock mechanism which records the induction period in hours. Results are given in Table IV. Figures for two commercially available inhibited oils are in addition compared with the corresponding base oils (BS 148 : 1951).

TABLE IV

Inhibited Oils

Description of oil	Sludge, %	Acidity, mg KOH/g	Induction period, hr
Oil A (BS 148 : 1951) .	0·018	0·18	0·5
+ 0·3% 24M6B . .	0·030	0·11	8·0
+ 0·3% 4M26B (DBPC)	0·029	0·21	23·0
+ 0·3% PBN . .	0·024	0·11	9·8
Oil B (BS 148 : 1951) .	0·023	0·18	0·6
+ 0·25% 24M6B . .	0·034	0·22	2·6
+ 0·25% PBN . .	0·046	0·19	2·9
Inhibited oil ex supplier A .	0·029	0·07	11·0
Base oil ex supplier A .	0·028	0·15	0·5
Inhibited oil ex supplier B .	0·015	0·07	9·1
Base oil ex supplier B .	0·013	0·15	0·5

Each figure is the mean of two determinations.

It can be seen that the test, when the standard conditions are employed, shows little promise of being suitable for assessing inhibited oils, if it is accepted

that the results given for induction period by the accelerated test can be taken as some measure of the relative performance to be expected from the oils in service. The sludge results for the inhibited oils are equal to, or higher than, those for the corresponding base oils, and there is little correlation between the results for sludge and induction period. The acidity results for the inhibited oils are lower, however, than for the corresponding base oils, excepting those oils with the shortest induction periods. It seems, therefore, that the acidity of the oil after oxidation might be related to the efficacy of an inhibited oil, but the difference between results for inhibited and uninhibited oils is not large enough to allow much confidence to be placed in them.

It is suspected that the increase in the sludge results for inhibited oils is due to the oxidation products of the inhibitor being thrown out of solution under the conditions of the test. The effect on inhibited oils of increasing the time of the test and of using soluble catalysts is discussed in the following section.

EXPERIMENTS UNDER MODIFIED CONDITIONS

The values for sludge and acidity obtained on conventional oils are low and represent a stage in oil deterioration corresponding to a fraction of the expected service life of the oils. A greater degree of deterioration could be attained by increasing the length of the test, or by using catalysts. Both methods have been briefly investigated.

Effect of Increasing Time

Fig 3 illustrates the effect of increasing the time of the test on sludge and acidity produced by an oil complying with BS 148 : 1951 (oil A) and experimental insulating oil 1. It can be seen that to obtain results approximating to those at which an oil is judged to have reached the end of its service life, a test period of at least 72 hours would be necessary. However, for the two oils in question it can be seen that the results at 24 hours are in the same proportion as those at 72 hours, so that there would appear to be little virtue in increasing the length of the test in these instances.

TABLE V

48-hour Test on Inhibited Oil

Description of oil	Sludge, %	Acidity, mg KOH/g	Induction period, hr
BS 148 : 1951 oil . .	0·098	0·35	0·5
+ 0·3% 4M26B . .	0·126	0·41	15·0

It can also be seen that the results for acidity appear to be more erratic than those for sludge.

It appeared possible that a differentiation could be made between inhibited and non-inhibited oils by increasing the time of test. Results of a 48-hour test are given in Table V for a BS 148 oil before and after adding 0·3 per cent of 4-methyl-2,6-di-*tert*-butylphenol (4M26B or DBPC). It can be seen that no distinction can be made between inhibited and non-inhibited oils by this means.

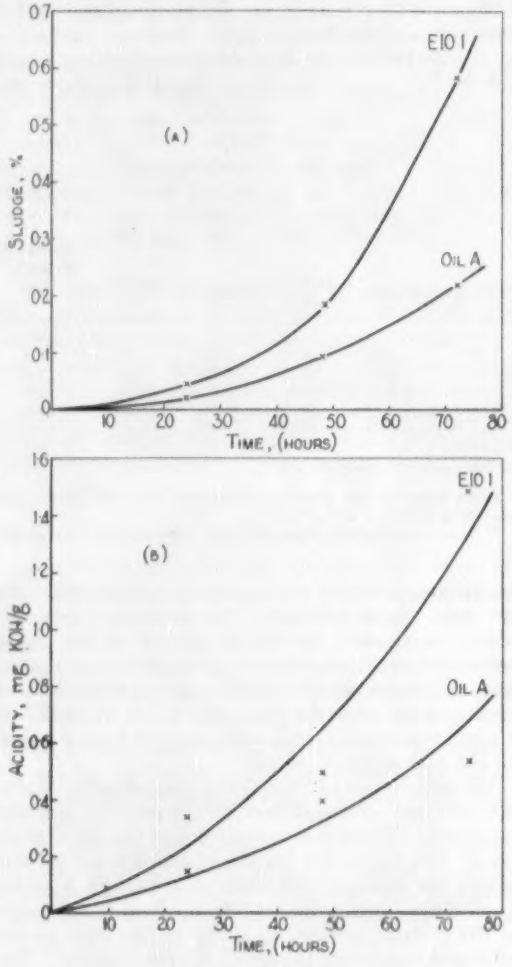

FIG 3

EFFECT OF LENGTH OF TEST ON (*a*) SLUDGE, (*b*) ACIDITY

Effect of Catalysts

The effect of catalysts was briefly investigated using a BS 148 : 1951 oil and E.I.O. 1. The oils were tested under the standard conditions, apart from the addition of the catalysts. Solid copper and shim steel were used in the form of rectangular sheets 2 × 1¼ inches, corresponding to a catalyst–oil ratio of 0·65 cm²/ml. The copper sheet was A.R. quality, 0·005 inch thick. The steel was 0·015 inch thick. The sheets were prepared and rolled into the form of cylinders as required for the copper catalyst in the oxidation test described in BS 148 : 1951. Oil-

soluble catalysts in the form of copper and iron naphthenates, supplied by the Thornton Research Centre of the Shell Petroleum Co., containing 6·80 per cent copper and 5·82 per cent iron, respectively, were used. A concentration of 5 p.p.m. metal was used in the tests. Results are given in Table VI.

TABLE VI

Effect of Solid and Soluble Catalysts

Oil	Quantity measured	Catalyst				
		None	Solid copper	Solid iron	5 p.p.m. copper	5 p.p.m. iron
A (BS 148 : 1951)	Sludge, % Acidity, mg KOH/g	0·021 0·15	0·052 0·26	0·030 0·21	0·056 0·29	0·048 0·22
E.I.O. 1	Sludge, % Acidity, mg KOH/g	0·047 0·34	0·26 0·90	0·053 0·36	0·060 0·38	0·069 0·37

Each figure is the mean of two determinations.

The results show that, as might be expected, both solid and soluble catalysts could be used to accelerate the oxidation. Copper metal has a pronounced effect on the oxidation of both oils, and it is significant that the " under-refined " oil is affected to an appreciably greater extent than the BS 148 oil. Iron metal has a slight effect on Oil A but practically none on E.I.O. 1.

The soluble-copper and iron catalysts have about the same effect on both oils. 5 p.p.m. soluble copper has about the same effect on oil A as the solid copper. E.I.O. 1, however, is much more sensitive to the copper metal.

The effect of copper and iron naphthenates as catalysts on the oxidation of inhibited oils is illustrated by the figures in Table VII. Results are given for a BS 148 oil alone and inhibited with 0·3 per cent 4-methyl-2,6-di-*tert*-butyl-phenol in the presence of 10 p.p.m. copper, 10 p.p.m. iron, and a mixture of 5 p.p.m. copper and 5 p.p.m. iron. Results for a 48-hour test with no catalyst are included for comparison.

There is a marked difference in the results for sludge between the straight and inhibited oil, but not in the acidity values, when copper, and a mixture of copper and iron, are used as catalysts. When iron alone is used, there is a marked difference in results for both sludge and acidity. The agreement between duplicate results was good in all instances. It is evident that the use of soluble catalysts allows a distinction to be made between inhibited and non-inhibited oils and that it might be possible to develop the test to evaluate inhibited oils. However, since increasing the length of the test to 48 hours has produced a greater degree of deterioration than have the catalysts and yet has not distinguished between the inhibited and the straight oil, it is not clear what part the catalysts are playing.

TABLE VII

Effect of Soluble Catalysts on Inhibited Oil

Oil	Catalyst						48 hours (no catalyst)	
	10 p.p.m. copper		10 p.p.m. iron		5 p.p.m. copper + 5 p.p.m. iron			
	Sludge, %	Acidity, mg KOH/g	Sludge, %	Acidity, mg KOH/g	Sludge, %	Acidity, mg KOH/g	Sludge, %	Acidity, mg KOH/g
A (BS 148 : 1951) . .	0·055	0·38	0·082	0·36	0·066	0·36	0·098	0·35
+ 0·3% 4M26B . .	0·024	0·30	0·029	0·16	0·033	0·32	0·126	0·41

Each figure is the mean of two determinations.

CONCLUSIONS

The high pressure oxidation method is simple in manipulation. The apparatus requires no attention during the oxidation period provided that the heating bath is reliable. The time required for preparation and sludge and acidity determinations is no greater than for other accelerated tests, that according to BS 148 : 1951 for example. It has the advantage over most other tests that the oxidation time is only 24 hours.

For intermittent testing it is particularly suitable, in that the apparatus can be easily stored and can be used at very short notice. There is no elaborate glass distribution system to collect dust or get broken when the apparatus is not in use. It is comparatively expensive, however; the cost of a bomb at the present time is about £80.

Although the acidity of the oil is not measured in the test as specified in ASTM D670–42T, it is considered that this measurement is useful and should be included in the test procedure.

The repeatability of results is satisfactory. Results obtained by one operator testing a British oil complying with BS 148 : 1951 using each of two bombs, indicated that a coefficient of variation of 10 per cent for sludge and 9 per cent for acidity should be ordinarily attainable, and with special care, using the same

crucible for filtering throughout, the figure for sludge could be reduced to 7 per cent. At the 5 per cent probability level these figures represent a repeatability of 28 per cent for sludge, expressed as a percentage of the mean, which may be reduced with special care to 18 per cent. The corresponding repeatability figure for acidity is 25 per cent.

Tests on a wide variety of oils, including new and reconditioned oils, a number of Continental oils, and a series of experimental insulating oils, indicate that the test will pick out oils which have been too heavily refined. It favoured an oil which was "under-refined" by the normally accepted standards, however. It appears to be very sensitive to small changes occurring in a new oil in storage.

It is not possible to distinguish between inhibited oils and the corresponding base oils, using the standard conditions of the tests. The use of copper and iron naphthenates as catalysts enables a clear distinction to be made, however.

The values for sludge and acidity obtained with conventional oils under the standard conditions of the test are low and represent a stage in oil deterioration corresponding to a fraction of the expected service life of the oil. Experiments have shown that a greater degree of deterioration can be obtained by using either solid or soluble catalysts.

ACKNOWLEDGMENTS

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HIGHER KETONES AS DEWAXING SOLVENTS*

By J. L. TIEDJE† and D. M. MACLEOD†

INTRODUCTION

A SOLVENT dewaxing plant using a pure ketone solvent, instead of the usual mixtures with benzene or toluene, has been operated by Imperial Oil Ltd. at its Sarnia refinery for about fifteen years. The laboratory investigations which led to the development of this process have been reported in papers by Pokorny and Stratford.[1] The actual operation of this unit was subsequently discussed by Mueller.[2] In view of the very satisfactory experience with higher ketone dewaxing at Sarnia, Imperial has recently been awarded a contract for the construction of a similar unit as part of a new lubricating oil plant at Edmonton. This paper discusses the main considerations involved in selecting a solvent for the dewaxing process and gives a laboratory evaluation of a series of higher ketones, which are also compared with the methyl ethyl ketone–aromatic mixtures as dewaxing solvents. It is concluded that some of the higher ketones show a definite performance advantage over the conventional M.E.K.–aromatic blends.

EVALUATION OF HIGHER KETONES AS DEWAXING SOLVENTS

In selecting a ketone for use as a dewaxing solvent, three major considerations are oil miscibility, wax solubility, and filter rate. A dewaxing solvent must be completely miscible with the oil being dewaxed at the temperatures and dilutions used in the dewaxing process. A good dewaxing solvent should also have the lowest possible solubility for wax, since a solvent of low wax solubility will permit dewaxing at higher temperatures for a given pour point oil, with a consequent saving in refrigeration costs. As the precipitated wax must be removed from the oil–ketone solution by filtration, a high filter rate is desirable. Most of the saturated aliphatic ketones meet other requirements, such as stability, non-corrosiveness, reasonably low boiling point, and low water solubility. Table I gives physical properties of the ketones investigated in this study.

TABLE I

Physical Properties of Aliphatic Ketones

	Mol weight	Boiling point, °F	D_4^{20}	n_D^{20}	Absolute viscosity, cp 20° C	Water solubility at 20° C		% water and b.p. °F of azeotrope		Flash point, °F
						Weight, % water	Weight, % ketone			
C_3 Ketone :										
Acetone .	58·08	133·7	0·791	1·3590	0·324	Complete	Complete	Non-azeotrope		15
C_4 Ketone :										
M.E.K. .	72·06	175·0	0·805	1·3791	0·425	11·59	27·33	11·0	156°	35
C_5 Ketones :										
M.nP.K.	86·08	215·6	0·811	1·3901	0·494	3·30	5·95	13·5	181°	—
M.iP.K.	86·08	203·0	0·810	1·3879	—	2·39	6·53	13·0	181°	—
D.E.K. .	86·08	216·1	0·815	1·3927	0·456	1·45	5·08	14·0	176°	55
C_6 Ketones :										
M.nB.K.	100·09	258·8	0·815	1·4007	0·626	2·12	1·75	Minimum b.p.		95
M.iB.K.[1]	100·09	242·2	0·802	1·3969	0·580	2·41	2·04	24·3	190°	75
C_7 Ketones :										
M.nA.K.	114·11	302·0	0·815	1·4007	0·795	1·31	0·44	48	—	—
M.iA.K.[2]	114·11	291·2	0·813	1·4060	—	—	—	—	—	—
D.nP.K.	114·11	291·4	0·817	1·4072	0·740	0·9	0·4	—	201°	105

[1] 4-Methyl-2-pentanone. [2] 5-Methyl-2-hexanone.

MISCIBILITY OF KETONES WITH OIL

Miscibility temperatures of oil–ketone mixtures are readily obtained in cases where an oil phase separates at a temperature above the wax point of the solution. However, when wax separates above the miscibility temperature, the determination is not so simple. In these cases it has been found possible to raise the miscibility temperature above the wax point by the addition of a lower molecular weight ketone. A series of miscibility temperatures obtained in this manner can be extrapolated back to zero concentration of the lower molecular weight ketone to give the required miscibility temperature. To be valid, this method requires that the miscibility temperatures of a

* MS received 6 October 1954.

† Imperial Oil Ltd, Canada.

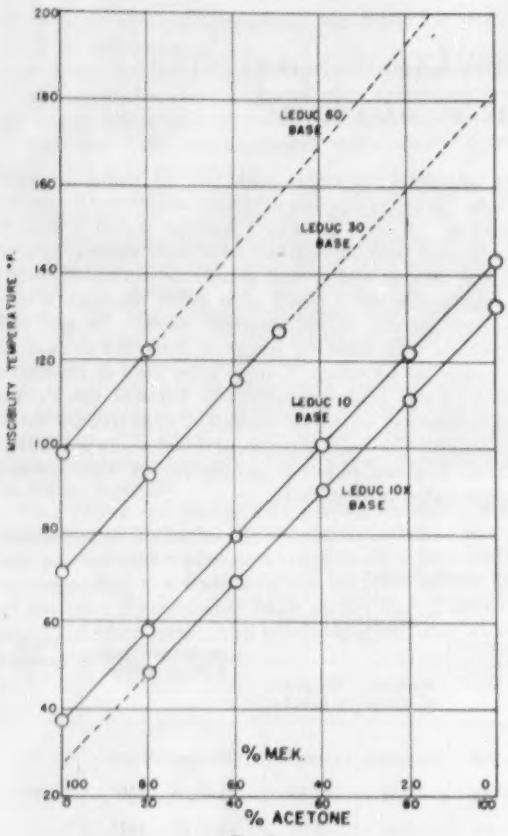

FIG 1

OIL MISCIBILITY

M.E.K–acetone mixtures 2 : 1 dilution ratio

given oil–ketone system be a linear function of the percentage of low molecular weight ketone in the solvent. This can be demonstrated over the full range of ketone concentrations in the case of the lower molecular weight ketones where miscibility temperatures occur above the wax point of a dewaxed oil. This is shown in Fig 1, for three different grades of lub oil diluted 2 : 1 with M.E.K.–acetone mixtures. The application of this technique to determine the miscibility temperature when below the wax point is shown in Fig 2.

Using the technique described above, miscibility temperatures of various ketones with 10, 30, and 60 grade lub oils have been determined at a 2 : 1 dilution ratio. Inspections on these oils are shown in Table II and miscibility data in Table III. Miscibility temperatures are shown in Fig 3 plotted against the number of carbon atoms per molecule for methyl normal ketones. As would be expected miscibility temperatures fall rapidly with increasing molecular weight. The C_5 ketones (M.P.K. and D.E.K.) are the lowest molecular weight ketones having miscibility temperatures which could permit dewaxing a 10 grade oil at

TABLE II

Lubricating Oils Used in Miscibility Measurements

Phenol treated and dewaxed distillates from Leduc crude

Lub base	Viscosity S.S.U. at 100	Viscosity S.S.U. at 210	Viscosity index	Pour/ solid, ° F
Leduc 60 .	1646	111·9	89·3	35/30
Leduc 60 [1] .	1827	117·0	69·1	−5/−10
Leduc 30 .	506	62·8	92·4	20/15
Leduc 10 .	154·6	43·1	89·3	10/5
Leduc 10X .	151·5	42·6	81·9	35/30
Leduc 10X [2]	170·0	43·3	70·1	−22 (solid)

[1] Dewaxed at −10° F. [2] Dewaxed at −25° F.

0° F or a 60 grade oil at 25° F. Moving the carbonyl group towards the centre of the ketone chain lowers the miscibility temperature. *iso*Ketones have miscibility temperatures which are 15° to 20° F higher than the corresponding normal ketones. As would be expected, heavy oils are less soluble in ketone and have higher miscibility temperatures than oils of lower viscosity. This effect decreases somewhat with increasing molecular weight of ketone.

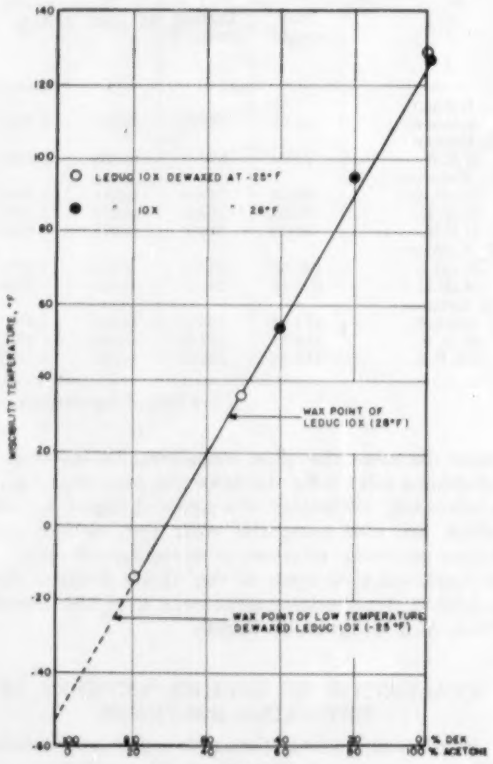
LEDUC 10X DEWAXED AT -25° F
" 10X " 28° F
WAX POINT OF LEDUC 10X (28°F)
WAX POINT OF LOW TEMPERATURE DEWAXED LEDUC 10X (-25°F)
MISCIBILITY TEMPERATURE, °F
% DEK
% ACETONE

FIG 2

DETERMINATION OF MISCIBILITY TEMPERATURE WHEN BELOW THE WAX POINT

Leduc 10X at 2 : 1 dilution ratio with D.E.K.

TABLE III

Miscibility Temperatures of 2 : 1 Mixtures of Ketones and Oils

Normal ketones		Leduc base oils			*iso*Ketones	Leduc base oils		
		10X	30	60		10X	30	60
C_3	Acetone	130	182	219	—	—	—	—
C_4	Methyl ethyl	27	71	98	—	—	—	—
C_5	Methyl propyl	− 37	− 1	18	Methyl*iso*propyl	− 21	+12	+33
	Diethyl	− 43	−15	4	—	—	—	—
C_6	Methyl butyl	− 63	−34	−18	Methyl*iso*butyl	− 60	−20	−10
C_7	Methyl amyl	− 95	−64	−50	Methyl*iso*amyl	− 73	−45	−28
	Ethyl butyl	−102	−67	−62	—	—	—	—
	Dipropyl	−106	−80	−62	Di-*iso*propyl	− 47	−15	− 6
C_8	Methyl hexyl	−122	−89	−72	—	—	—	—
	Ethyl amyl	—	—	—	Ethyl*iso*amyl	−105	−84	−72

Fig 4 shows that the miscibility temperatures were found to be constant over a fairly wide range of dilution ratios with methyl ethyl ketone. In the case of the 60 grade oil, little or no change in miscibility temperature occurred over the range of 1 to 3 dilution ratios. For the 10 grade oil this region of constant miscibility temperature shifted to between 0·5 to 2·5 dilution ratios. Outside these ranges, at both the higher and lower dilutions, miscibility temperatures decreased rapidly. The same effect has been found for diethyl ketone, and may be assumed to apply to other members of the series.

The effect of water on miscibility temperatures of oil–ketone solutions can be determined by direct measurement if these temperatures occur above the point of wax separation. A 60 grade oil was selected to evaluate this effect because miscibility temperatures are usually critical and are most easily determined experimentally with a high viscosity lub fraction. To eliminate wax interference, a sample of Leduc 60 base oil was dewaxed to $-5°/-10°$ F pour/solid. The effect of water on the miscibility temperature of 3 : 1 dilutions with M.P.K., D.E.K., and M.iB.K. is shown in Fig 5. In each case the first additions of water cause the oil miscibility temperature to rise about 30° F for each 1 per cent water, but at a certain water content the oil miscibility temperature reaches a maximum. Above this temperature with higher water contents, a water cloud is thrown out first, followed by an oil cloud at a lower temperature. The effect is seen most clearly when the maximum oil miscibility temperature is low enough to cause the free water to settle out in the form of ice, and the subsequent oil cloud may be easily observed, *e.g.* D.E.K. Similar results have been reported by Hall and McCarty for a Mid-Continent residuum and 40/60 M.E.K–benzene solvent.[3]

The initial linear increase in miscibility temperature may be explained by supposing that the miscibility temperature of water with oil is about 2800° to 3600° F, and that the oil miscibility temperatures of mixtures of water and ketone lie on the straight line drawn between the oil miscibility temperatures of pure ketone and pure water. This would be analogous to the relationship between the miscibility temperatures of an oil with two different ketones.

The maximum miscibility temperature results from partial dehydration of the solution before the oil cloud point is reached. Thus, if the miscibility temperature is plotted against per cent water in solvent, straight lines are obtained as shown in Fig 5 at low water concentrations. The plot of water miscibility temperature against per cent water in

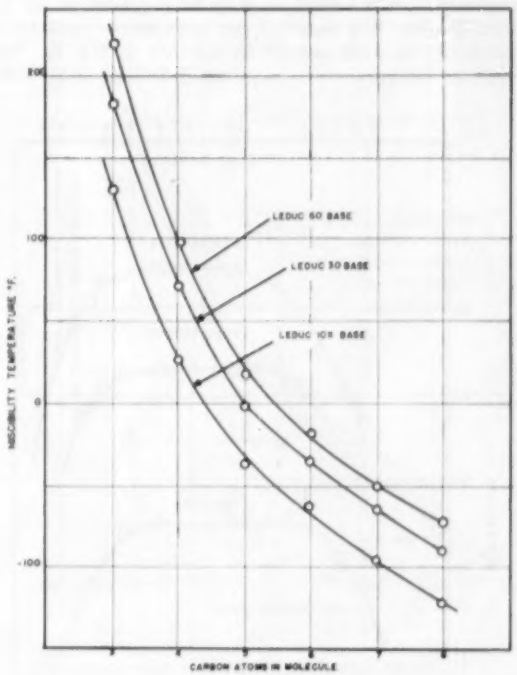

FIG 3

MISCIBILITY TEMPERATURE FOR METHYL NORMAL KETONES AND OIL

2 : 1 Dilution ratio

ketone for an oil–ketone solution would result in a curve cutting the straight line.

In Fig 5 the horizontal maximum temperature line does not show points of oil miscibility at higher dissolved water contents, but merely indicates the temperature at which the two lines intersect. These points actually represent check determinations of the temperatures of intersection of the water and oil miscibility curves.

The slope of the oil miscibility line and the maximum oil miscibility temperature were little affected by change in oil–ketone ratio over the range normally used in dewaxing. As would be expected, the water miscibility line was gradually displaced to lower water percentage by increasing the oil content.

The horizontal sections of the curves shown in Fig 5 represent temperatures above which an oil phase cannot separate regardless of how much water is present. To ensure adequate oil miscibility a ketone dewaxing solvent must be dehyrated to a low water content if dewaxing is to be carried out below the maximum miscibility temperature shown in Fig 5. These data indicate that if Leduc 60 is to be dewaxed at 25° F, dehydration to about 0·3 per cent water content is necessary to keep the oil in solution in M.P.K., but that no dehydration is required if D.E.K. or M.iB.K.

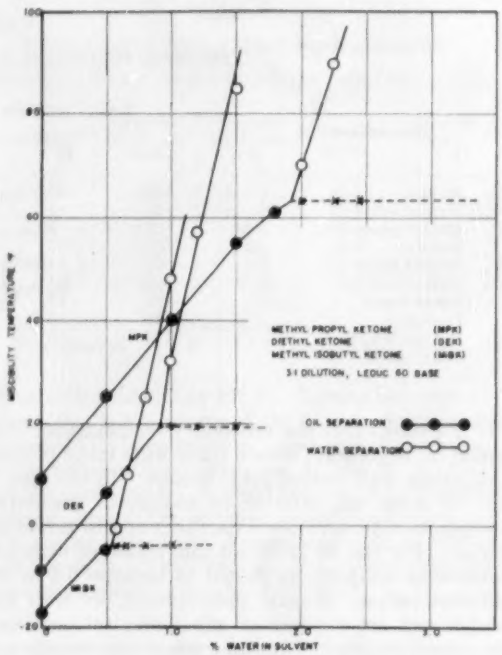

Fig 5

MISCIBILITY TEMPERATURES *vs* WATER CONTENT

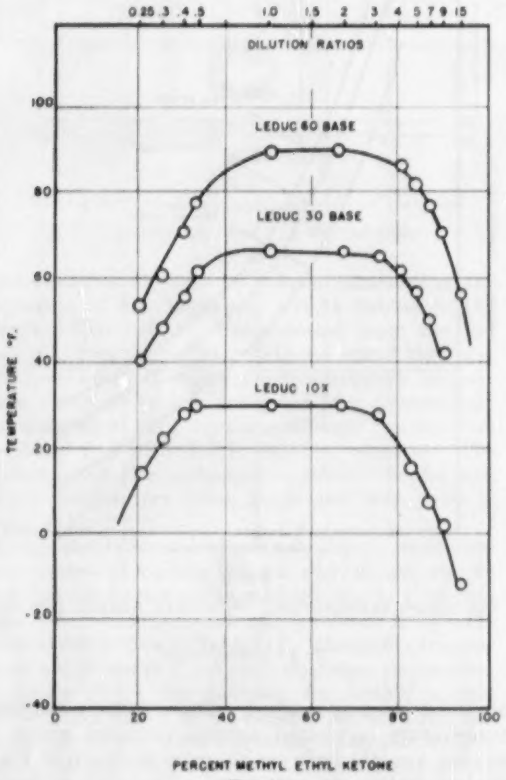

Fig 4

EFFECT OF DILUTION ON MISCIBILITY TEMPERATURE

are used as solvent. D.E.K. is borderline in this respect. However, as dehydration by azeotropic distillation is simple and effective in the case of higher ketones it is probably justified to reduce corrosion even in the cases where it is not necessary to ensure oil–ketone miscibility.

WAX SOLUBILITY

The temperature at which solvent dewaxing must be carried out to give an oil of the desired pour point is governed by the solubility of wax in the solvent.[1] Dilution also has some effect on the pour point, but this variable must be held within fairly narrow limits to obtain the best filter rates and is, therefore, of secondary importance. As refrigeration equipment and scraped surface chillers are major items of expense in a dewaxing plant, the solvent with the lowest wax solubility and the highest dewaxing temperature for a given pour point is preferred.

Although any type of wax could be used to compare solubilities in the various ketones at 110° F melting point recrystallized paraffin wax was selected as a reference for the following reasons:

(*a*) The higher solubility of a low melting point wax facilitates direct solubility measurements at dewaxing temperatures of 0° to 30° F without the extrapolations required when using a high melting wax.

(*b*) In solvent dewaxing, the presence or

absence of low melting waxes determines the pour point of a dewaxed oil.

The solubilities of a 110° F melting point wax in a series of ketones are shown plotted against temperature in Fig 6. Operating experience in Imperial's

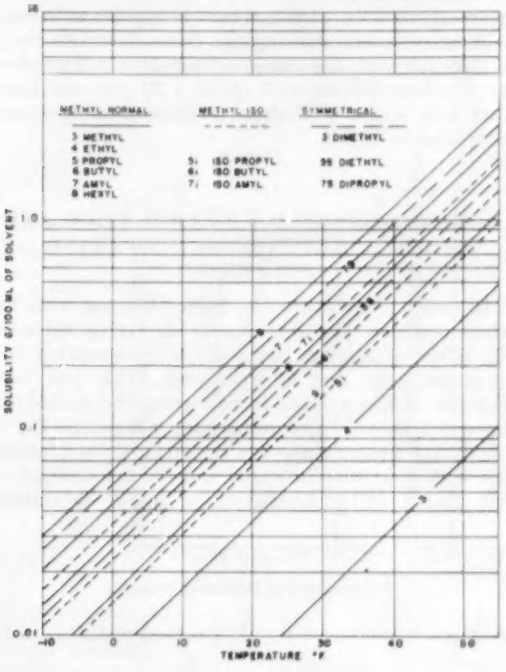

FIG 6

SOLUBILITY OF 110° F M.P. WAX IN ALIPHATIC KETONES

Sarnia plant over a period of years has shown that when dewaxing with methyl propyl ketone, the solid point of the dewaxed oil very nearly coincides with the dewaxing temperature. Assuming that M.P.K. gives a 0° F solid point when dewaxing a 10 grade distillate at 0° F, the other ketones shown in Fig 6 would give the same solid point at the temperature at which their wax solubilities corresponded with that of M.P.K. at 0° F. On this basis, dewaxing temperatures for 0° F solid points would be as follows :

	°F
Dimethyl (actone)	+30·5
Methyl ethyl ketone (M.E.K.)	+ 9·5
Methyl*iso*propyl	+ 1
Methylpropyl ketone (M.P.K.)	0
Methyl*iso*butyl ketone (M.iB.K.)	— 5
Diethyl (D.E.K.)	— 6
Methyl butyl ketone	— 8
Methyl*iso*amyl	—10
Methyl amyl	—13
Dipropyl	—16
Methyl hexyl	—19

From the standpoint of wax solubility alone, acetone and M.E.K. would obviously be first and second choices as dewaxing solvents. However, both of these ketones are unsatisfactory because of poor oil solubilities (high miscibility temperatures). Of the ketones having satisfactory miscibility temperatures, the propyl ketones show the lowest wax solubilities, followed by *iso*butyl and diethyl ketones, which require 5° and 6° F lower dewaxing temperatures respectively than methyl normal propyl ketone.

The data shown in the above tabulation are plotted in Fig 7. It will be noted that for a given molecular weight, *iso*ketones would permit the highest dewaxing temperatures followed by the methyl normal and finally the symmetrical ketones, *e.g.* dewaxing temperatures for the C_5 ketones would be in the order : M.iP.K. M.P.K. D.E.K.

In the case of M.P.K. and D.E.K. solvents which are 6° F apart for equivalent wax solubilities. Operating data from Imperial's Sarnia dewaxing plant have closely checked predictions based on solubilities. Because solid points of dewaxed oils are difficult to reproduce with sufficient accuracy, a difference of this magnitude can be detected only by averaging a large

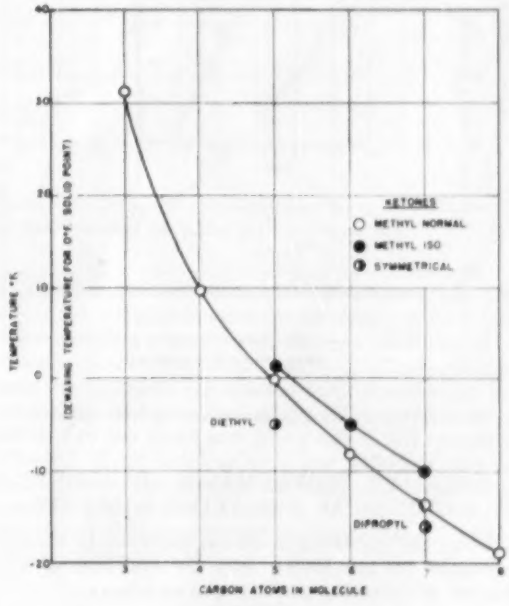

FIG 7

TEMPERATURE FOR EQUIVALENT WAX SOLUBILITY

Reference methyl propyl ketone at 0° F

number of determinations. Average data for the spread between dewaxing temperatures and solid points in the Sarnia dewaxing plant may be summarized as follows :

	°F
100 per cent M.P.K.	0·7
75/25 D.E.K/M.P.K.	3·8
90/10 D.E.K/M.P.K.	5·5

FILTER RATES

Dewaxing filter rates for a series of higher ketones have been compared in the laboratory using a sample of Leduc 30 distillate diluted with 2·5 volumes of ketone. This slurry was chilled from solution temperature to 25° F at a rate of 7° F/minute prior to filtration. Filter rates were found to be a function of molecular weight and independent of ketone structure. The rapid drop in filter rate with increasing molecular weight is shown graphically in Fig 8.

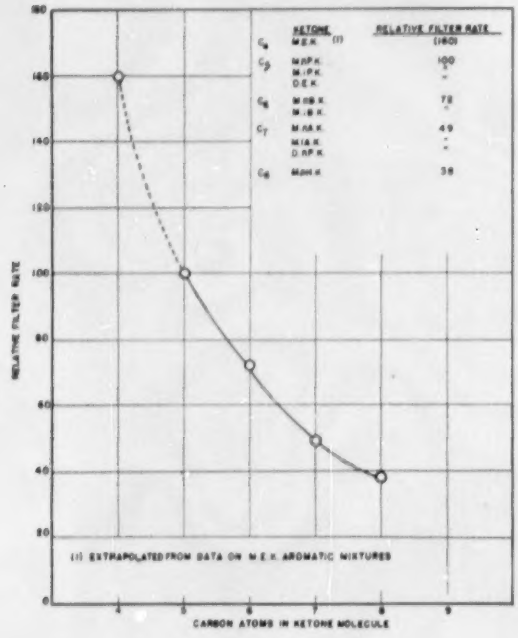

FIG 8

COMPARISON OF FILTER RATES FOR HIGHER KETONES

RELATIVE PERFORMANCE OF HIGHER KETONES AS DEWAXING SOLVENTS

From the preceding sections, the ketones showing adequate oil miscibility may be summarized with respect to dewaxing performance as follows:

Ketone	Relative filter rate	Temperature for equivalent wax solubility
C_5: Methyl-*n*-propyl (M.P.K.)	100	0
Methyl*iso*propyl	100	+ 1
Diethyl (D.E.K.)	100	− 6
C_6: Methyl-*n*-butyl	72	− 8
Methyl*iso*butyl (M.iB.K.)	72	− 5
C_7: Methyl-*n*-amyl	49	−13
Methyl*iso*amyl	49	−10
Dipropyl	49	−16

It will be noted that the methyl propyl ketones appear to be the best dewaxing solvents, having the highest filter rate and lowest wax solubility. Methyl-*iso*propyl ketone shows a slight advantage over *n*-propyl in terms of wax solubility but its oil miscibility would not be adequate, *e.g.* 33° F with a 60 grade lub, for a plant processing high viscosity stocks at relatively low temperatures. Diethyl ketone appears to be next in order of merit, showing the same filter rate but a 6° F penalty in dewaxing temperature. Methyl*iso*-butyl ketone follows with about a 30 per cent lower filter rate and a 5° F drop in filtering temperature compared to M.P.K.

COMPARISON OF M.E.K.–AROMATICS AND HIGHER KETONES AS DEWAXING SOLVENTS

In order to compare the higher ketones with the more common M.E.K–aromatic dewaxing solvents, the effect of solvent composition on dewaxing performance must first be evaluated. This has been done for M.E.K–toluene blends using the techniques described above. The results are plotted in Fig 9. Miscibility temperatures are shown for three reference oils with anhydrous solvents and for the limiting oil (60 grade) under conditions of water saturation.

TABLE IV

Performance of Dewaxing Solvents

Solvent	Temperature for equal wax solubility	Relative filter rate	Dewaxing 60 grade oil to 25° F pour point		
			Dewaxing temperature, ° F	Miscibility temperatures, ° F	
				Anhydrous	Saturated
Higher ketones:					
M.P.K.	0	100	25	18	63
D.E.K.	− 6	100	19	4	19
M.iB.K.	− 5	72	20	−10	−4
M.E.K.–Aromatics:					
70/30	− 4	100	21	22	68
65/35	− 7	92	18	11	44
60/40	−10	82	15	0	21
55/45	−12·5	73	13	−11	5
50/50	−15	63	10	−21	<5

Relative filter rates are shown with M.P.K. as a reference. Wax solubilities are compared as temperatures for solubilities equivalent to that of M.P.K. at 0° F.

Table IV summarizes performance factors for M.E.K–aromatic blends and the three most attractive higher ketone solvents. In the case of the blends, filter rates and wax solubilities improve with increasing M.E.K. contents, but miscibility temperatures show the opposite effect. As an efficient dewaxing operation is not practical below the oil miscibility temperature, miscibility will be the critical factor in determining what M.E.K–aromatic solvent must be used.

In order to compare the blended solvents with higher ketones, a specific situation must be considered. Unless a dewaxing plant is capable of changing solvent composition to suit each stock processed, the solvent will likely be fixed by the most viscous oil processed. Dewaxing temperatures and relative filter rates have been predicted for various solvents used to dewax a 60 grade lub distillate to 25 solid point. These results, as well as dry and saturated miscibility temperatures for the same oil, are shown in the last three columns in Table IV. This table indicates that any of the higher ketones shown will perform in a satisfactory manner. Water content is critical only in the case of M.P.K. Although this solvent shows the highest dewaxing temperature and best filter rate, dehydration to a low water content is necessary to maintain the oil in solution. In the case of the blended solvents 70 per cent M.E.K. and 30 per cent toluene is equivalent to M.P.K. in filter rate, but shows a 4° F penalty in dewaxing temperature. However, this solvent would be borderline with respect to oil miscibility even with anhydrous solvent. If the M.E.K–aromatic dewaxing is carried out with a saturated solvent, as is generally the case, Table IV indicates that 55 per cent M.E.K. would be necessary. This solvent would show a 27 per cent reduction in filter rate and a 12° F penalty in dewaxing temperature when compared with M.P.K.

CONCLUSIONS

It is concluded that some of the higher ketones show better performance as dewaxing solvents than M.E.K–aromatic mixtures. The actual magnitude and value of this improved performance depends on a comparison of the two types of solvent in a specific refining situation. The particular stocks to be processed will determine the composition of the M.E.K–aromatic blend required. When this is known, improvements in filter rates and dewaxing temperatures for a higher ketone can be readily determined.

In designing a new plant, the cost of dewaxed oil capacity obtained through the use of a higher ketone must be balanced against the cost of obtaining the same capacity by expanding the chilling and filtering sections of the plant and using an M.E.K–aromatic solvent. If an existing unit has sufficient solvent recovery capacity, the gains in refrigeration and filter capacity obtained by changing to a higher ketone should result directly in higher charge rates or higher yields of dewaxed oil.

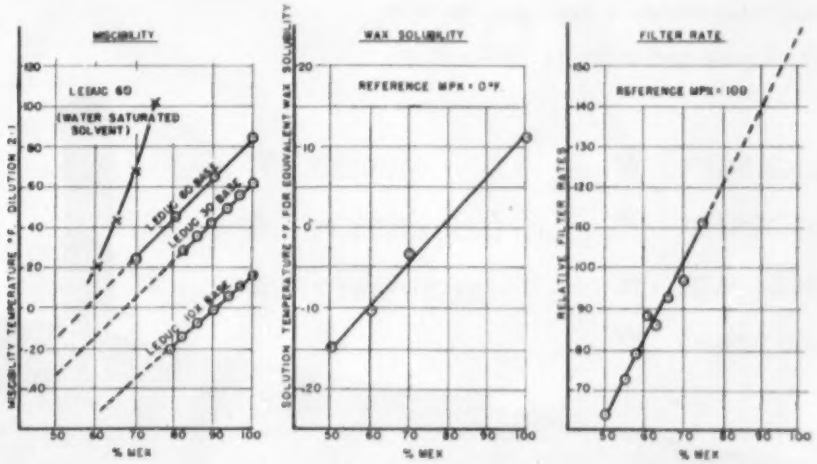

FIG 9

EFFECT OF SOLVENT COMPOSITION ON THE DEWAXING PERFORMANCE OF M.E.K–TOLUENE MIXTURES

References

[1] Pokorny, O. S., and Stratford, R. K. *J. Inst. Petrol. Tech.*, 1937, **23**, 746, 750 and *Oil Gas J.*, 1938, **36**, 96.
[2] Mueller, A. J. *Oil Gas J.*, 1940, **38**, 54, 56.
[3] Hall, F., and McCarty, B. Y. *Nat. Petrol. News*, 1937, **29**, R15.

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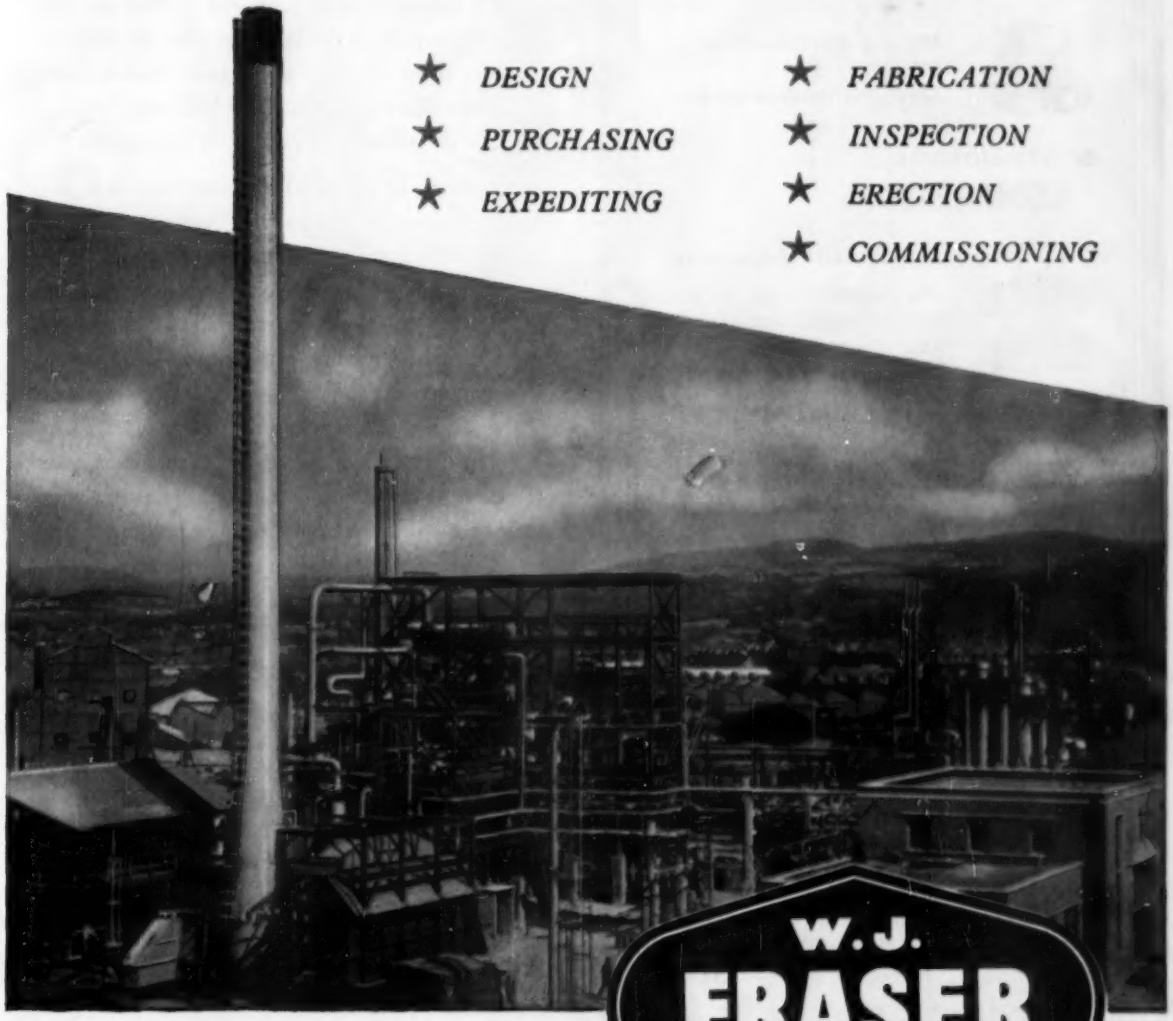

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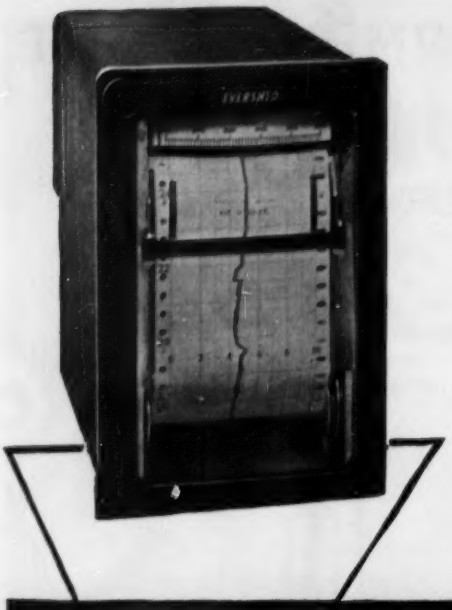

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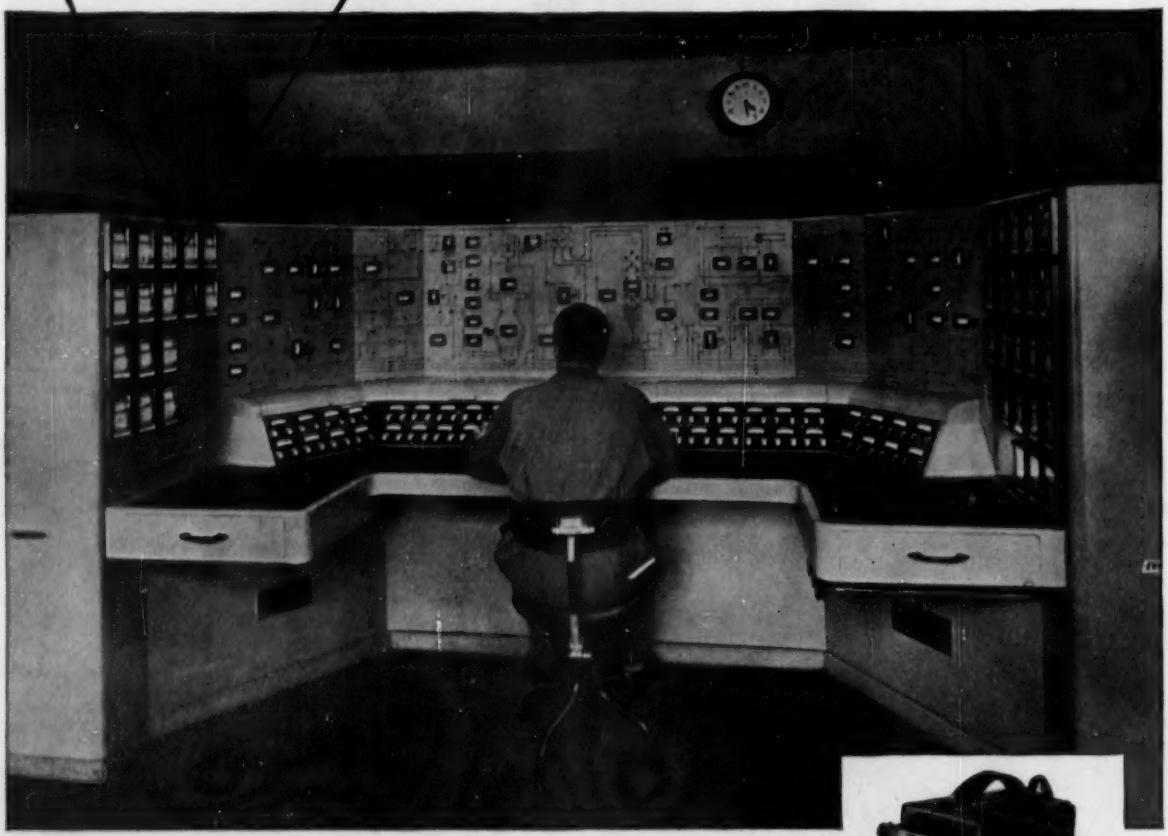

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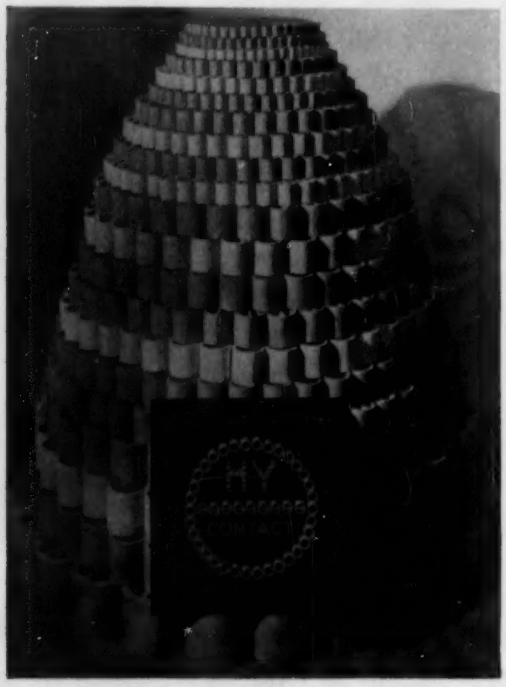

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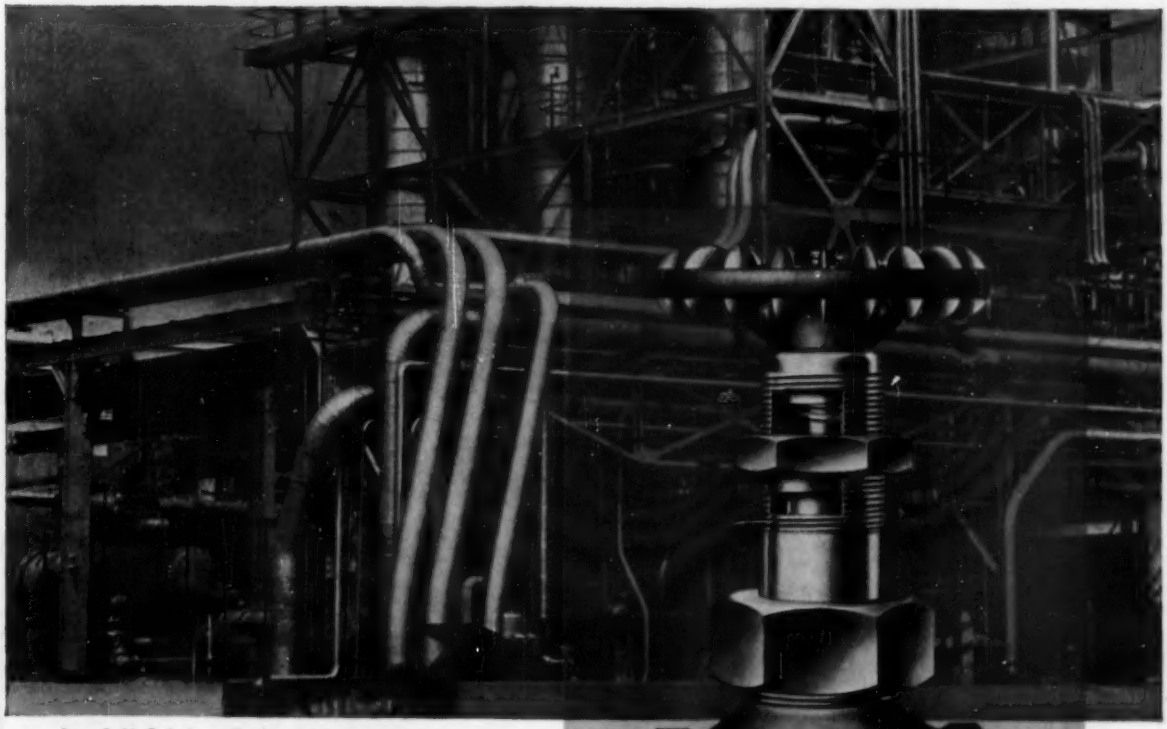

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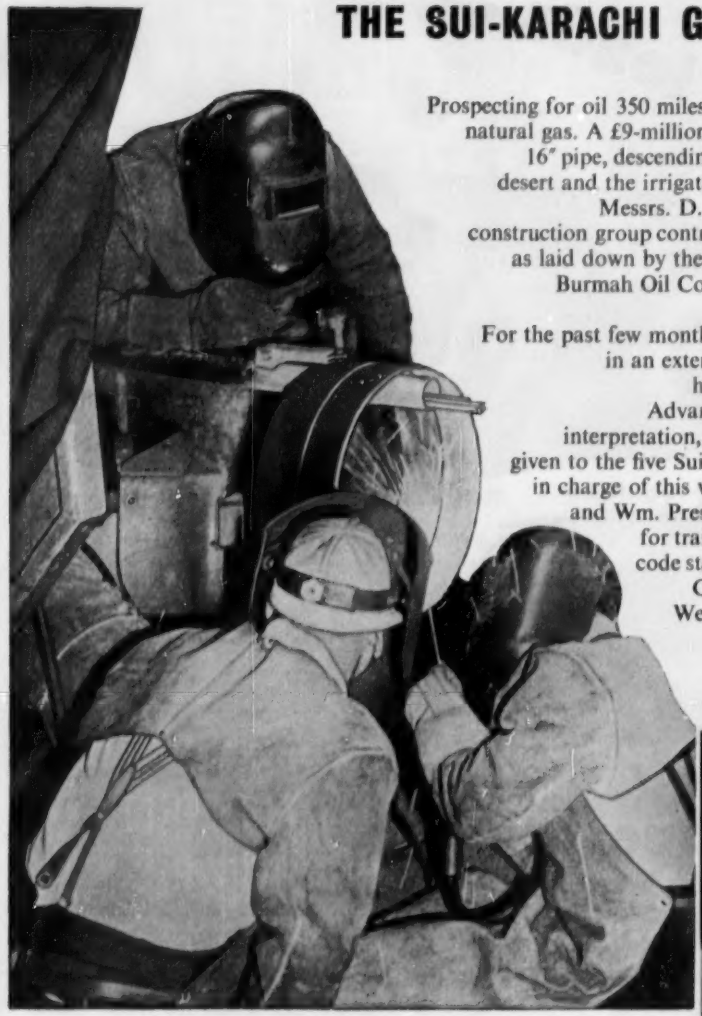

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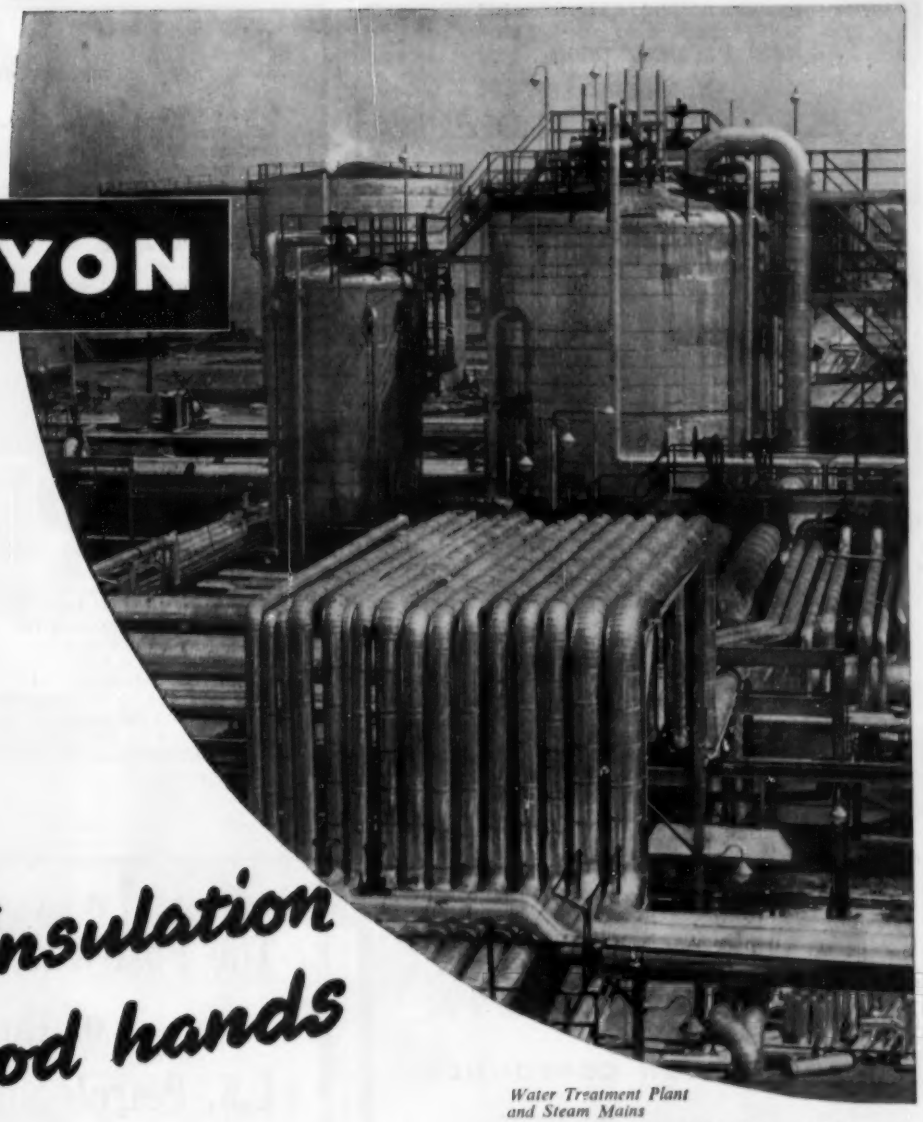

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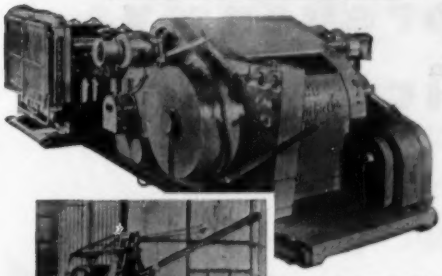

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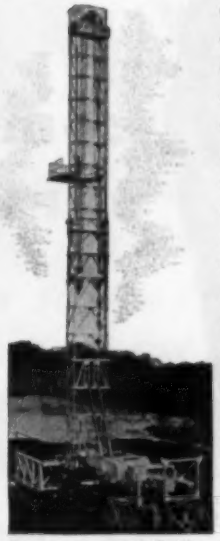

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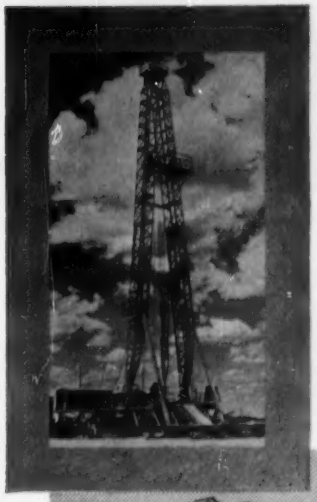

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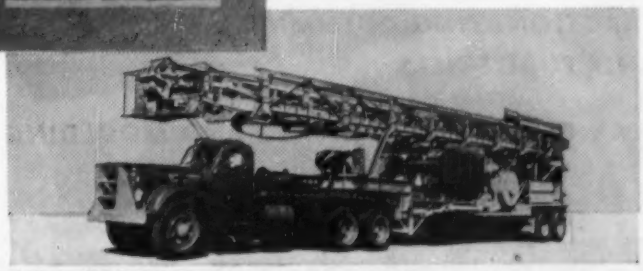

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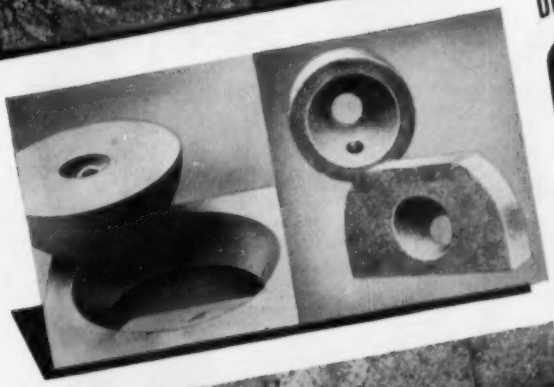

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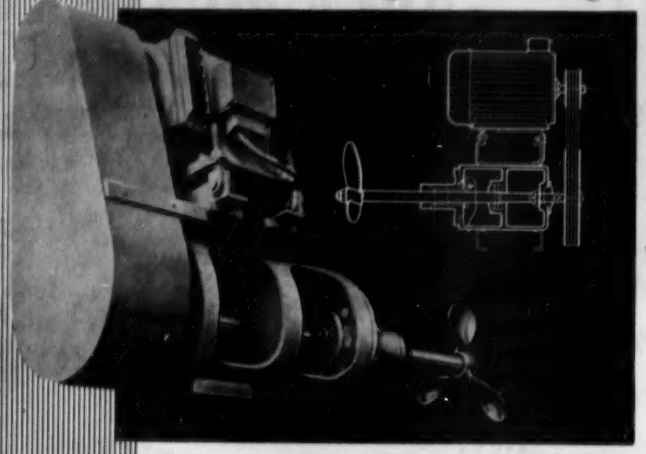

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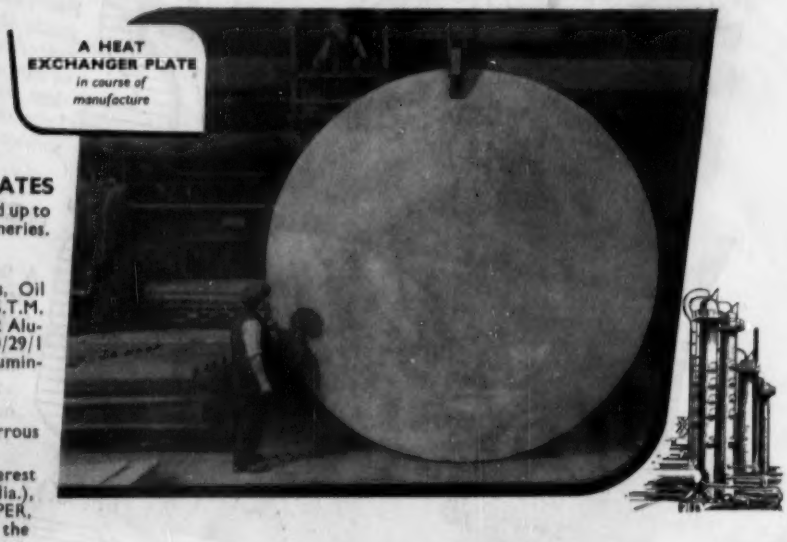

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